Evaluation of the
Limited Engineering Scale Testing of the CEROX™ Process
To Treat NSCMP Neutralents

Prepared for:

Non-Stockpile Chemical Materiel
Program Manager

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Stone & Webster™
A Shaw Group Company

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EXECUTIVE SUMMARY

This report evaluates the results of the Limited Engineering Scale Tests of the CerOx™ Process. Stone & Webster, Inc. conducted these tests on behalf of Non-Stockpile Chemical Material Program (NSCMP) (Edward F. Doyle, Alternative Systems Demonstration and Evaluation Group Leader) to evaluate the applicability of the process to the treatment of NSCMP neutralents. The tests were conducted from May 21st to June 8th, 2001, utilizing a CerOx System 2 Unit installed at the University of Nevada, Reno (UNR), Reno, Nevada.

Two NSCMP MEA-based neutralent simulants were tested: HD (distilled sulfur mustard) neutralent simulant and GB (sarin) neutralent simulant. The technology was evaluated based on four test objectives. The conclusions are summarized below for each listed objective.

1. **Demonstrate stable operability at maximum continuous throughput.**
   - The CerOx System 2 showed stable operation and processed 1.4 and 2.4 kg/hr of HD neutralent simulant and GB neutralent simulant respectively for up to 24 hours.
   - The liquid effluent generated consistently fell below the 25 ppm TOC (Total Organic Carbon) test criteria and generally ranged from 2 to 6 ppm TOC.
   - Estimates of overall destruction were based on the most reliable data, namely TOC concentrations on influents and effluents. The results of these calculations showed destruction efficiencies which ranged from 97 to 99%.
   - During the validation testing, stack gases were estimated at 71-73 dscfm, scrubber effluent ranged between 0.6 and 1.5 gpm, and generated solids amounted to less than a couple of grams recovered from the anolyte solution.
2. **Demonstrate the fate of relevant heteroatoms (F, Cl, S, and P) contained in the feed material.**
   - The data gathered were insufficient to determine elemental material balances for relevant heteroatoms due to analytical difficulties and inaccurate flow measurements.
3. **Provide basic engineering data to evaluate practicality for implementation in NSCMP.**
   - The test data show that a CerOx System 2 of the configuration tested, modified to address certain concerns identified (see below), could process about 2500 gallons of NSCMP HD neutralent or about 4300 gallons of NSCMP GB neutralent per year assuming 80% stream factor.
   - The CerOx System 2 tested is best described as an early commercial system used for research purposes, which did not reflect the best design for the destruction of NSCMP neutralents. This unit initially showed some instability, which was quickly recognized and corrected. CerOx was able to run two 24 hour continuous tests under stable operations, one for each feed. Shortcomings in the tested system included inadequate Gas Phase Reactor and off-gas treatment designs. CerOx latest generation technology, of which a System 4 has been manufactured and delivered to UCI, addresses these design issues.
4. **Quantify and document key operating and engineering design parameters.**
   - The CerOx technology could be designed to process waste equivalent to the production rate of expected NSCMP neutralents. Scale up is directly proportional with area of the electrodes in electrochemical cells. The scale up of other core technology, including the Liquid and Gas Phase Reactors, would be by residence time using standard engineering practices and fundamentals. During operation, temperature, pH, cerium +3/+4 concentration, acid concentration, cell voltage, etc. require monitoring, but very little control.

During the testing, there were a number of issues that developed or were identified. The key ones are listed below:

- In two of the test runs, 0.69 to 1.9 mg/L 1,2-dichloroethane (DCE) was reported in the liquid effluent. DCE is regulated as a toxic contaminant under RCRA's TCLP at a concentration of 0.5 ppm or greater. The CerOx System Liquid and Gas Phase Reactor has since been modified to increase the

system's ability to destroy VOCs such as 1,2-dichloroethane. Based on the test results, the liquid effluent generated by the CerOx System (with modifications) is likely to require minimal, if any, treatment prior to discharge. Note that DCE is an ingredient in the simulant feed and is not expected to be found in the actual NSCMP HD neutralent.

- CerOx Test data show that small quantities (less than a couple of grams) of solids are recovered in the anolyte solution. There was insufficient data to characterize these solids for RCRA requirements. This must be addressed in future testing.
- Stack gas velocities were measured using a single pito tube with questionable accuracy. The stack gases were adjusted based on the carbon mass balance.
- No NSPS or NESHAPs or its associated MACT standards have been established that would apply directly to the CerOx technology. If it is assumed that the NESHAP for Hazardous Waste Combustor (MACT standards) would apply to the CerOx System 2, then CO, THC, HCl and Cl_2 would all fall below their respective allowable limits and none would be considered a major HAP source. Modifications to the existing design are required to increase the efficiency of the Gas Phase Reactor, NOx Absorbers, and Acid Gas Scrubbers to further reduce the emissions of THC, NOx, HCl, and Cl_2 that could come from a NSCMP application. CerOx has stated that such modifications have been incorporated in the recently manufactured CerOx System 4, which was purchased by the University of California, Irvine. A new source of NOx equivalent to the CerOx system tested would not typically be significant enough to trigger major source permit and control technology requirements.
- Process wastes are generated including anolyte and catholyte solutions. These electrolyte solutions would be considered characteristic hazardous wastes and would have to be recycled/reclaimed or disposed of by a facility permitted under RCRA to receive and treat hazardous wastes. The tests performed did not attempt to determine the useful life of the anolyte and catholyte solutions, but were changed between test campaigns per the test plan.
- The data gathered to determine destruction efficiency were insufficient due to analytical difficulties and inaccuracies in flow measurement.

Based on the test results, it is recommended that a detailed evaluation of the latest generation CerOx technology be performed to determine if issues identified during the testing have been addressed and if further testing is appropriate.

Evaluation of the Limited Engineering Scale Testing of the CEROX™ Process To Treat NSCMP Neutralents

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1. Introduction

This report evaluates the results of the Limited Engineering Scale Tests (LEST) of the CerOx™ Process. Stone & Webster, Inc. conducted these tests to evaluate the applicability of the process to the treatment of Non-Stockpile Chemical Materiel Program (NSCMP) neutralent feeds.

The tests were conducted from May 21st to June 8th, 2001, utilizing a CerOx System 2 Unit installed at the University of Nevada, Reno (UNR), Reno, Nevada. Table 1-1 summarises the actual test runs completed using neutralent simulant feeds.

Table 1-1 Test Summary

Test	HD Neutralent Simulant				GB Neutralent Simulant			
	HD-1	HD-2	HD-3	HD-4	GB-1	GB-2	GB-3	GB-4
Test Type	Work-up	Validation	Validation	Validation	Work-up	Validation	Validation	Validation
Date	23-May-01	23-May-01	30-May-01	24-May-01 25-May-01	01-Jun-01	01-Jun-01 02-Jun-01	04-Jun-01	05-Jun-01
Test Duration, hrs	4	8	8	24	4	8	8	24

The CerOx System 2 unit is housed in the Environmental Health and Safety (EH&S) Annex Building on the UNR Campus. The Annex Building is dedicated to UNR's waste management activities including, handling, consolidation and shipping of chemical or hazardous waste.

CerOx, with the participation of UNR, performed the tests under a subcontract to Stone & Webster, Inc. Stone & Webster provides technical support for the NSCMP under their Program and Integration Support Contract. Stone & Webster subcontracted TRC Environmental Corporation and Southwest Research Institute (SwRI) for sampling and analytical services in support of the testing.

This section discusses the objectives of the LEST and the Evaluation Criteria that Stone & Webster developed to evaluate the test's performance. Section 2 of this report provides a summary of Stone & Webster's technology evaluation efforts and the CerOx Process. Section 3 describes the CerOx System 2 unit that was tested. Section 4 describes all of the test runs completed as part of the LEST. The results of the tests are presented in Sections 5 and 6. Section 5 includes a discussion of the operability of the CerOx System 2 Unit. Section 6 presents the analytical results of the samples collected during testing. Sections 7 and 8 include the test conclusions and recommendations for further action.

1.1 Objectives and Evaluation Criteria

The overall objective is to perform testing to determine the applicability of the CerOx Process system to treat NSCMP neutralents.

The proposed test was designed to provide results, which will allow determination as to whether the specific test objectives have been met. Table 1-2 lists the specific test objectives coupled with evaluation criteria.

Table 1-2 Test Objectives & Evaluation Criteria

Test Objective	Evaluation Criteria
1. Demonstrate, at maximum continuous throughput, stable operability of the CerOx System for each feed material.	• Continuous stable operation with all systems controlled and no system function overridden for the duration of the tests. • Target destruction efficiency of at least 99% with less than 25 ppm TOC in liquid effluent • Liquid effluents meet limits for disposal from Federal Wastewater Treatment Facility • Solid residuals can be disposed of at RCRA facility • Gaseous effluents are permittable
2. Determine the fate of relevant heteroatoms contained in the feed material during operation of the CerOx System.	• Material balance closure for Fluorine, Chlorine, Sulfur, Phosphorous, and Cerium. • Overall material balance for process unit
3. Provide basic engineering data to evaluate the CerOx System practicality for implementation in the NSCM Program	• Projected system size • System operating characteristics • System safety including engineered safeguards • Reliability, availability and maintainability • Fabrication and operational costs • Ability to obtain a permit for the process
4. Quantify and document key operating and engineering design parameters to support conceptual design package	• Documentation of key operating parameters, critical scale-up parameters and core technology scale-up philosophies which support conceptual design packages

2. BACKGROUND

2.1 Technical Background

The CerOx™ technology is a Mediated Electrochemical Oxidation (MEO) process that uses cerium ions to oxidize organic compounds. The low temperature, low pressure CerOx™ Process is part of a family of metal-ion-catalyzed processes developed by the Pacific Northwest National Laboratory (PNNL)[1] for organic destruction. In 1995, CerOx Corporation (then known as EOSystems Inc.) obtained exclusive worldwide rights from PNNL (expires 2018) to use the patented[2] (US Patent 5,707,584) cerium process for the destruction of hazardous organic compounds.

The CerOx™ System is a skid-mounted; self contained, fully automated organic-waste treatment unit consisting of modules of patented[3] T-CELLs™. CerOx manufactures T-CELLs™ and assembles them into self-contained, transportable systems.

In 1997 CerOx built and delivered its first CerOx™ unit, a CerOx™ System 4 (nameplate capacity of 55 gallons per day) to the University of Nevada at Reno (UNR) to perform research projects to destroy liquid laboratory waste[4]. In 1999, the system was retrofitted with two T-CELLs™ manufactured with injection-molded parts to change the configuration from a four cell arrangement to a two cell arrangement. These modifications converted the System 4 into a System 2, which would have a nameplate capacity of 25 gallons per day of waste. In the determination of nameplate capacity, waste is defined as having approximately 50% organic content. The System 2 is operated under the provisions of the University's existing air and water discharge permits. CerOx also supplied a pilot-scale unit to the Naval Surface Warfare Center, Crane, IN, for testing on propellants, energetics, and other waste materials.

The CerOx™ Systems are designed to process liquid waste, but CerOx has indicated that the process could be modified and developed to treat slurries and to decontaminate metal surfaces.[5] The CerOx System 2 does not, however, currently have these capabilities.

2.2 Historical Background

The U.S. Army Program Manager for Chemical Demilitarization (PMCD) established the Non-Stockpile Chemical Materiel Program (NSCMP) with the mission to provide centralized management and direction to the Department of Defense for the disposal of non-stockpile chemical materiel in a safe, environmentally sound and cost effective manner. The NSCMP includes five categories of chemical warfare materiel (CWM): binary chemical weapons; former production facilities; miscellaneous CWM; recovered chemical weapons; and buried CWM. Substantial differences exist between CWM in the Stockpile and Non-Stockpile programs. Whereas the stockpiled CWM is present in larger quantities, non-stockpile CWM encompasses a greater variety of materiel with far more physical configurations and agent-fill types. The variety, locations and deteriorated physical condition of non-stockpile CWM pose unique requirements for treatment systems.

To support accomplishment of its mission, the NSCMP developed an Overarching Research Plan (ORP) which establishes the goals, requirements, and approaches for evaluating and developing technologies for the safe and efficient disposal of non-stockpile CWM. The ORP identifies systems that NSCMP has and is continuing to develop to meet its mission goals. The ORP also identifies additional needs and associated schedule to support accomplishment of these goals.

To meet these needs, NSCMP has identified several additional systems for application to non-stockpile CWM based on the results of technology evaluations and demonstration testing performed as part of the PMCD Alternative Technologies and Approaches Program (ATAP) and the Assembled Chemical Weapons Assessment Program (ACWAP). To meet the ORP goals, NSCMP has determined that engineering design data is required to support full-scale implementation of CWM treatment systems.

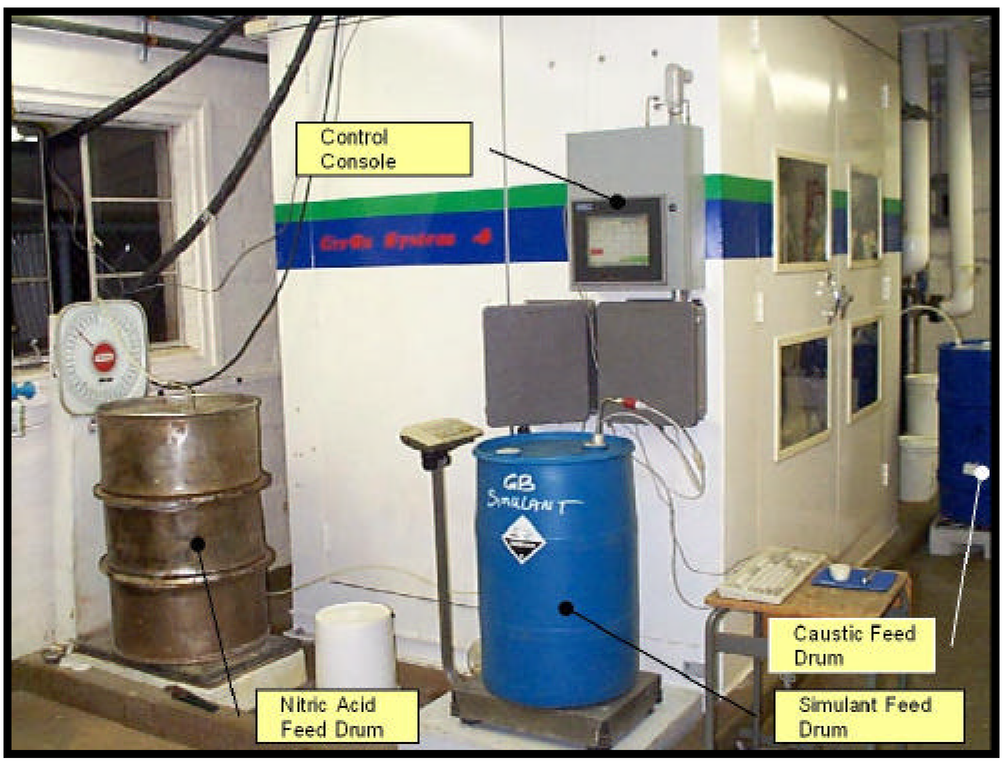
In November 2000, NSCMP identified CerOx Mediated Electrochemical Oxidation process as one of the technologies for which engineering design studies are to be performed to support full-scale implementation. Stone & Webster contacted CerOx in December 2000 on behalf of NSCMP (Edward F. Doyle, Alternative Systems Demonstration and Evaluation Group Leader) and inquired about a test program to treat NSCMP neutralents. In March 2001, Stone & Webster placed a subcontract with CerOx to perform the Limited Engineering Scale Testing of the CerOx Process.

3. SYSTEM DESCRIPTION

The Limited Engineering Scale Testing of the CerOx Process to treat NSCMP neutralents was performed utilizing a CerOx System 2 installed at the University of Nevada at Reno (UNR), Reno, Nevada. This unit, which has been used to research the destruction of organic wastes (such as Polychlorinated biphenyls, dioxins, chlordane, kelthane, and pemethrin) and has been modified from its original design to reflect process requirements and implement improvements. The System 2 used for the LEST has a 6'x8' footprint and 9' in height (Figure 3-1). The System 2 consists of the following main systems, which are shown on the Process Flow Diagram (Figure 3-7 and Figure 3-8):

- Electrochemical Cell System
- Cerium-4 Reactors & Waste Feed Systems
- Off-gas Treatment & Neutralization
- Utilities & Support Systems (not shown on Process Flow Diagrams - PFDs)

Figure 3-1 CerOx System 2 at UNR



3.1 Electrochemical Cell System[6]

3.1.1 Electrochemical Cells

The electrochemical cell assembly consists of two identical cell packs with each cell pack constructed of two end plates, one end electrode-cathode, one end electrode-anode, nine bipolar, and ten Nafion® membrane plates assembled to produce ten electrochemical cells (Figure 3-2). The cell housing is made of polyvinylidene fluoride (PVDF). Each electrode anode surface is platinum plated on the titanium base.

Each cell pack is powered via two anode and cathode connection terminals protruding through the end plates from the respective anode and cathode plates. Both cell packs are connected electrically in series from power supply leads and bus bar connections. Each cell pack is equipped with a voltage indicator.

A high voltage alarm on either of the cell packs will result in the shutdown of the entire system. If the combined voltage of the two cell packs exceeds the DC power supply's capacity or the systems set point, then the power supply will automatically reduce the current to the level supported by that voltage.

Figure 3-2 Electrochemical Cell Schematic

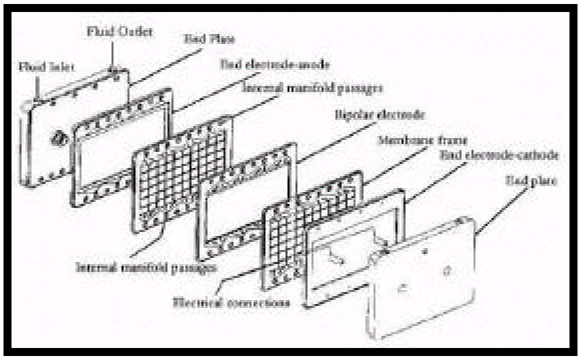
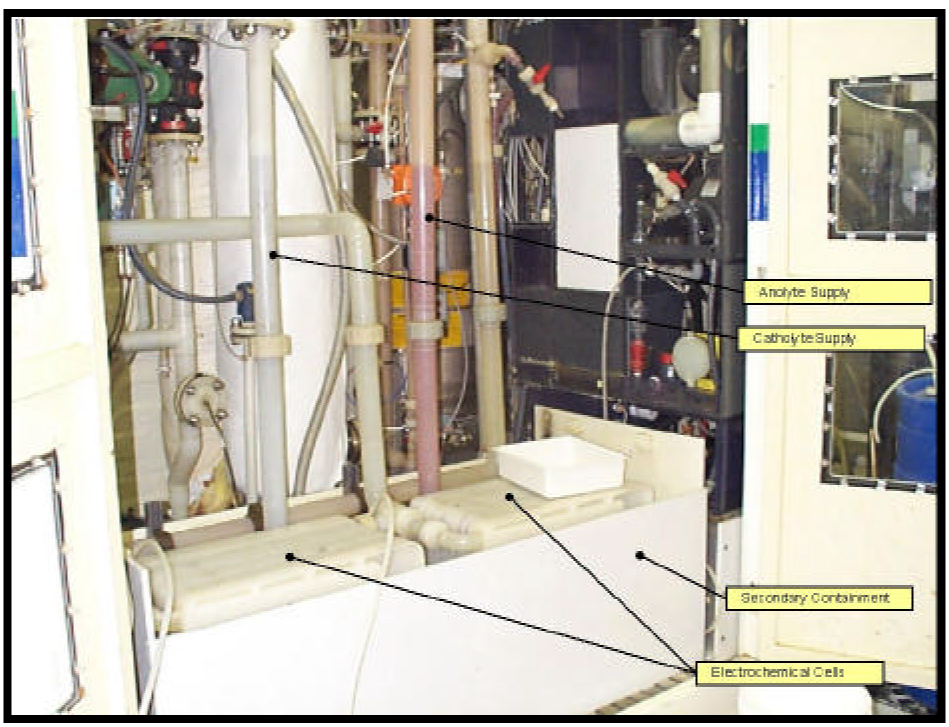


Figure 3-3 Electrochemical Cells



3.1.2 Anolyte Recirculation and Supply Loop

The Anolyte Supply Pump P-120 (PVDF, PTFE wetted parts) supplies anolyte solution to the electrochemical cells and the reactor system from the Anolyte Tank, TK-120 (Titanium). This tank also receives return flow from both the electrochemical cells and the Liquid Phase Reactor. The Anolyte Tank is equipped with a continuous level element to monitor the level of anolyte solution. The level element is programmed with low-level and high-level alarm set points.

Flow rate of anolyte solution to the electrochemical cells is measured by a flow meter and regulated by a manually adjustable shutoff valve. A low flow rate of anolyte from the pump is detected by a flow meter and activates a low flow set point, which shuts down the pump. Differential pressure between the anolyte and catholyte solutions is monitored using a differential pressure element. Anolyte absolute pressure to the electrochemical cell assembly is monitored using a pressure element. A low-pressure or high pressure condition in the anolyte system triggers low or high alarms which results in the shutdown of pump P-120 which in turn will shutdown all systems associated with the electrochemical cells and reactors. The temperature of anolyte returning from the electrochemical cell to T-120 is monitored using a temperature element.

3.1.3 Catholyte Recirculation and Supply Loop

The Catholyte Supply Pump, P-110 (PVDF, PTFE wetted parts), supplies catholyte solution to the electrochemical cells and the NOx Absorption Columns C-310 and C-320 (316SS) from the Catholyte Tank, TK-110 (316SS). This tank also receives return flow from both the electrochemical cells and NOx Absorption system. The Catholyte Tank is equipped with a continuous level element to monitor the level of catholyte solution. The level element is programmed with low and high level alarm set points.

The flow rate of catholyte solution to the electrochemical cells is controlled with a control valve, which is regulated by the output from the catholyte tank level. Catholyte absolute pressure to the electrochemical cell assembly is monitored with both low-pressure and high-pressure alarm positions which will result in the shutdown of pump P-110 which in turn will shutdown of all systems associated with the electrochemical cells, absorbers and reactors.

Heat generated by the electrochemical cell system is removed via the Catholyte Heat Exchanger, HX-110 (316SS), located on the NOx absorber loop. Heat generated on the anolyte side, is transferred to the catholyte via heat exchange across the bipolar electrode plates within the electrochemical cell assembly. Both the heat exchanger inlet and outlet temperatures of the catholyte are monitored.

Note that the Reactor Offgas Condenser, HX-210 (316SS), was moved after the first two LEST validation tests, into the catholyte circulation loop where it was used as a trim cooler to HX-110, as shown in Figure 3-8. The flow of cooling water to the heat exchanger is controlled with a flow control valve, which was controlled by the temperature set point on the Catholyte Tank (TK-110).

The catholyte flow returning from the electrochemical cell carries NOx gases generated by the electrochemical process. These off gases are cooled via a Vent Condenser, HX-111 (316SS), integrally mounted on the vent outlet of the catholyte tank. The cooled NOx off gas temperature is monitored. Condensate from HX-111 returns to TK-110. Cooling water flow rate to the vent condenser is manually adjusted using a hand control valve.

Catholyte acid strength is monitored by a conductivity sensor and is maintained within prescribed concentrations by subsequent on/off control of the Nitric Acid Addition Pump, P-401 (wetted parts 316SS and PTFE), not shown.

3.1.4 Cell Assembly and CerOx System Unit Containment

Secondary liquid containment is provided for the electrochemical cell assembly for the purpose of confining any potential leaks from the cell packs (Figure 3-3). The polypropylene secondary containment consists of a box like structure, which supports the cell packs and provides hydraulic and electrical interface connection feed-through. The box is equipped with two redundant leak detectors. Activation of either leak detector results in the complete shutdown of the electrochemical cell and associated systems.

The base structure is equipped with an integrally constructed sump equipped with a leak detector. Activation of the leak detector results in a complete shutdown of the CerOx system.

3.1.5 DC Power Supply

Direct current power is supplied to the electrochemical cells from a high efficiency, current limiting, DC power supply capable of supplying up to 500 amperes at 175 volts. The DC power supply normally operates in a current control regime. The power supply delivers the pre-set current to the cells using the appropriate voltage value to maintain this current. However, if the applied potential (voltage) required to supply the desired current attempts to exceed the voltage limit, the current will drop to the level that will be supported by the limiting voltage. The power supply is equipped with a current control input and voltage and current monitor outputs. In addition, separate inputs are provided to turn the DC power on and off and contacts provided to indicate DC power on. A power supply temperature sensor with high alarm contacts is also provided. The power supply internal over temperature limit switch shuts down the power supply should it overheat. A shutdown of the DC power supply is interlocked to a complete shutdown of the organic feed supply pump (P-201) to the reactor system.

Figure 3-4 Power Supply

3.2 Reactor & Waste Feed System

In standard operations waste organics are fed from a 55-gallon drum (DR-200) which is placed on a secondary containment platform and connected to the Waste Organic Metering Pump, P-201 (wetted parts PTFE, ceramic). For the tests, the drum was placed on a drum scale to verify mass flow rates. Flow rate of the organic waste is initially set using a calculation derived from an algorithm employing operator input of system parameters via the keypad interface. The calculated flow rate is determined and a control signal for initial pump operating speed is established. Control of the organic feed rate is based upon the rate at which Ce^{+4} concentration changes. The analyzer control loop adjusts the organic feed rate via speed adjustment of pump P-201. The Ce^{+4} analyzer is programmed with a low alarm set point, which, if activated, terminates the operation of P-201. For these tests, the sample valves were inoperable due to malfunction in previous tests due to improper materials of construction. Samples of the anolyte were taken manually to monitor the concentration of Ce^{+4}. New set points for the organic feed rate were manually entered and were based on the Ce^{+4} concentrations.

3.2.1 Reactor Systems

The organic waste reactors consist of a Liquid Phase Reactor, TK-210 (titanium), and a Gas Phase Reactor, TK-220 (titanium with ceramic packing) (US Patent 5,968,337). The Liquid Phase Reactor effectively treats water soluble organics and finely dispersed, immiscible organics with boiling points greater than the normal operating temperature of the system (~100°C). The Gas Phase Reactor treats gas phase organics and low boiling point immiscible or miscible feed stocks when introduced into the system.

Organics are injected into the fresh anolyte solution flow going to the Liquid Phase Reactor, TK-210, at a point just prior to the Sonic Mixer, SM-211. The Anolyte Supply Pump, P-120, supplies Anolyte solution to the Liquid Phase Reactor. An orifice plate regulates flow rate to this reactor. After combining with the organic waste, the anolyte flow enters the sonic mixer.

The sonic mixer is operated continuously when organic feed is initiated. The mixer is most effective when processing immiscible components, which require dispersion in order to provide a higher effective surface area for the oxidation reaction to proceed. In this LEST, the sonic mixer was not utilized because the HD and GB neutralent simulants were miscible in the anolyte solution. After the anolyte solution and organic waste feed are combined within the sonic mixer the solution enters the Liquid Phase Reactor and flows upward for the prescribed hydraulic residence time (approximately 12 minutes) prior to overflowing to the Anolyte Tank, TK-120. The chemical oxidation of the organic waste results in the evolution of CO_2, unreacted gaseous organic components (including volatile intermediate products and volatile organic compounds in the waste stream), and chlorine (Cl_2) gas if chlorine is present in the organic molecule being treated. The reaction gas exits the Liquid Phase Reactor and is routed to the inlet of the counter current Gas Phase Reactor where it is contacted with fresh anolyte solution in a packed bed (ceramic Norton Intelox). Within the Gas Phase Reactor, unreacted gaseous organic compounds are oxidized. The anolyte effluent from the Liquid Phase Reactor combines with that of the Gas Phase Reactor from the Reactor Recirc Pump, P-220 (PDFE, PTFE wetted parts), via level control, where the flow back to the Anolyte Tank, TK–120.

Fresh anolyte solution is supplied to the Gas Phase Reactor from the anolyte tank by the supply pump P-120. A flow control valve regulates the anolyte flow rate to the Gas Phase Reactor, which is monitored by a flow element. The descending anolyte flows counter-current to the organic vapors and reaction-product gases in the packed column reactor. Spent anolyte accumulates in the Gas Phase Reactor base and is transferred via pump, P-220, to the anolyte tank, T-120. The anolyte level is controlled within the Gas Phase Reactor using level control valve and level element to control the transfer rate of the transfer pump, P-220.

Control of the organic reactors is achieved through maintenance of preset flows of anolyte solution to the liquid and Gas Phase Reactors and through monitoring the spent anolyte solution's Ce^{+4} concentration in the effluent of the Liquid Phase Reactor. The anolyte temperature from the Liquid Phase Reactor is also monitored prior to its return to the anolyte supply tank. Normally, the feed rate of the organic waste stream is controlled based upon maintenance of a prescribed set point for the concentration of Ce^{+4} in the effluent of the Liquid Phase Reactor. In LEST validation tests, the concentration of Ce^{+4} was monitored manually via titration. The Ce^{+4} analyzer is programmed with a low concentration alarm set-point which stops all organic feed to the system, by shutdown of P-201, if activated (not activated for performed tests).

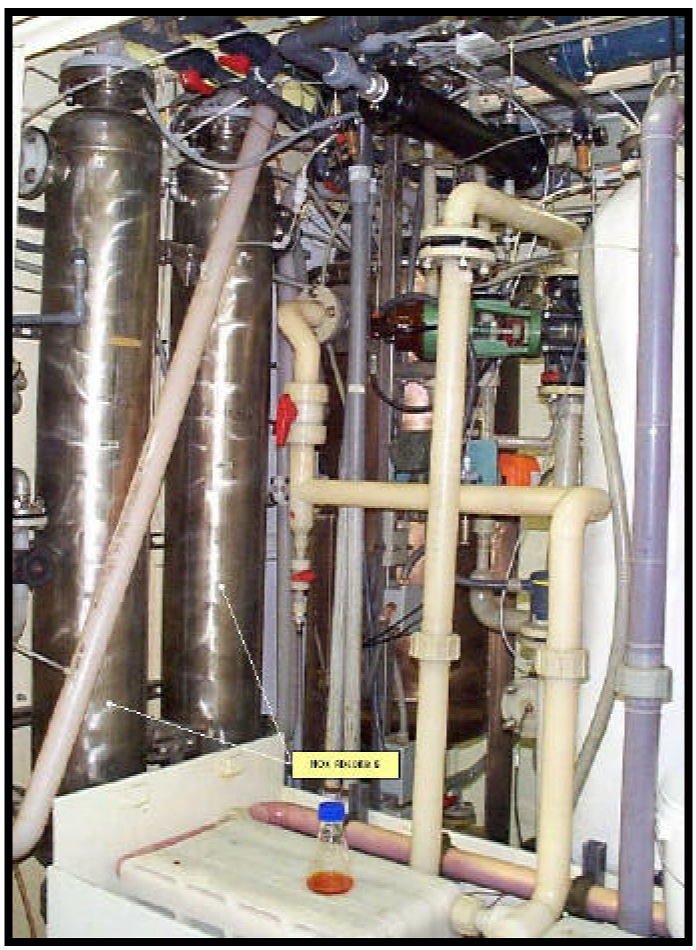
The original design (Figure 3-7) routed all reaction off-gases through a condenser, HX-210, and cooled to minimize residual water and nitric acid carryover content prior to entering the Axi-Shear off gas scrubber system, XX-330. Temperature of the cooled off gas was monitored via temperature element TE-212. For the first two validation tests of the LEST, no cooling water was supplied to HX-210 because CerOx has experienced very little benefit in operating the condenser. HX-210 was subsequently moved for the final 4 LEST validation tests to provide trim cooling for the catholyte loop (see descriptions above and Figure 3-8).

3.3 Off gas Treatment and Neutralization System

3.3.1 NOx Absorption System

Nitrogen oxide gases, produced by the cathode reaction of nitric acid, are vented from the Catholyte Tank, cooled and routed to the NOx Absorption columns for recovery of nitric acid value (see Figure 3-5). Air is introduced in the incoming NOx gas flow to promote the oxidation of NO to NO_2. The airflow is set with a manually adjustable regulating valve and monitored by rotometer.

Figure 3-5 NOx Absorbers



The NOx system consists of two packed (Intalox saddles) 316SS absorption columns operated in series. Gas enters the bottom of the first column and contacts recirculated nitric acid solution in a counter current configuration across the packed bed. The effluent gas from the first column exits the top and are routed to the bottom of the second column where it again contacts a recirculating stream of dilute nitric acid in an identical column configuration. The absorption column nitric acid flow is counter current to the NOx gas flow. Weak nitric acid is routed to the top of the absorption columns where it falls via gravity through the packing and contacts the up-flowing NOx gases, absorbing NO_2 to form nitric acid. The nitric acid product from the absorption columns is returned to the Catholyte Tank. The oxidation of NO with O_2 (Eq. 1) and NO_2 absorption with water to form HNO_3 (Eq. 2) is shown below:

$$(1)\ 2NO + O_2 \rightarrow 2NO_2$$

$$(2)\ 3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

The absorption columns share a common collection manifold for the electrolyte. Control of liquid flow rates to balance liquid inventory and prevent column flooding is accomplished through the use of a level controller coupled to level control valve for which bleeds the excess catholyte back into TK-110. The level control is programmed to stop the Column Recirc Pump, P-310 (PVDF wetted parts) should the low-low set point be activated.

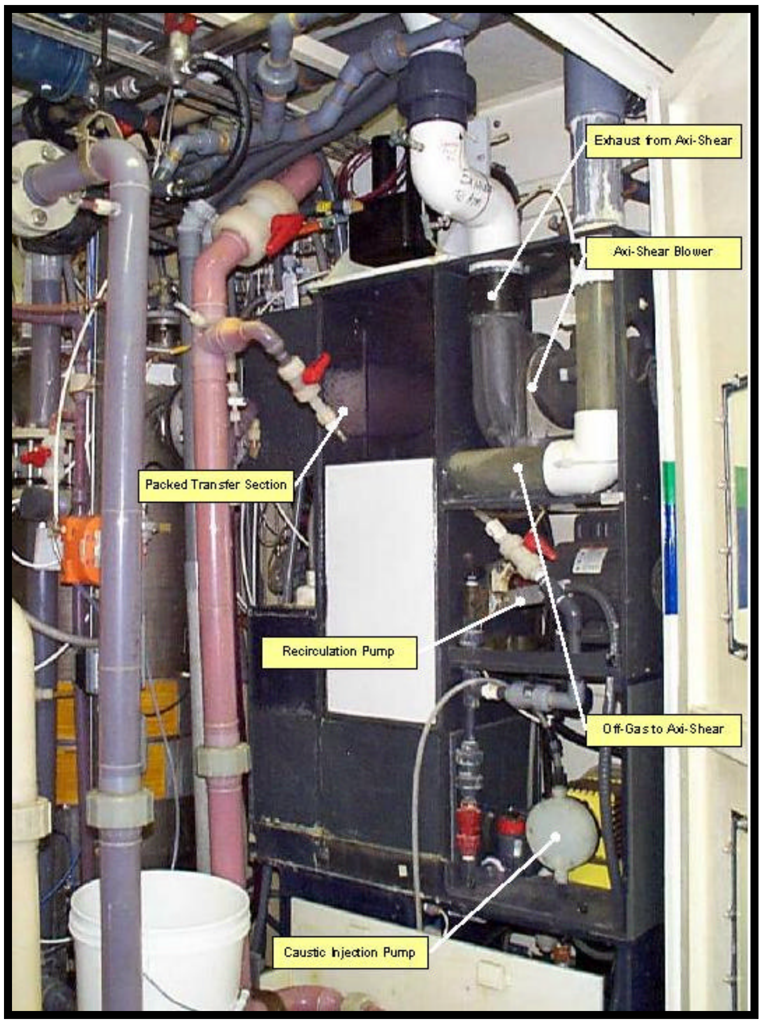
The NOx tail gas, which exits the second absorption column, is monitored for temperature and routed to the NOx Caustic Scrubber (C-330). The NOx Caustic Scrubber is a counter current packed column with tail gas entering the bottom and recirculating caustic solution entering the top. The purpose of the scrubber is to remove NOx content from the tail gases. The caustic recirculating system consists of a NOx Caustic Scrubber Drum (DR-3XX, 55-gallon drum) and a NOx Caustic Scrubber Circulation Pump (P-3XX). This system is located adjacent to the main CerOx unit. The scrubber solution is periodically charged to the drum and there are no automatic controls associated with the NOx Caustic Scrubber System. The tail gas from the scrubber is sent to the Axi-Shear scrubber unit for final treatment and neutralization of residual NOx content.

Operational failure of any primary component (C-310, C-320) in the NOx absorption system results in a shutdown of the system and subsequent shutdown of the electrochemical cell and all associated dependent equipment until corrective action is taken and system performance can be re-established. Operational failure of any equipment in the NOx Caustic Scrubber (C-330) is not part of any shutdown system.

3.3.2 Axi-Shear Scrubber System

The Axi-Shear scrubber unit, XX-330, is provided to remove acid gases from the reaction off gas stream and from residual NOx gases from the NOx Caustic Scrubber tail gas prior to release to the atmosphere. The scrubber system is supposed to remove chlorine and nitrogen oxides and neutralize these acid gases through contact with a sodium hydroxide solution. The resultant neutralized aqueous solution is normally discharged to the local sewer which leads to the local POTW via Discharge Pump, P-332 (PP wetted parts). During the LEST, resultant neutralized aqueous solution was stored in a wastewater collection tank prior to disposal to the same local sewer. The tail gases from the Axi-Shear unit are discharge through a centrifugal blower to the off-gas stack. The centrifugal blower has no flow or speed controls. In order to provide a sufficient volume of air through the Axi-Shear unit under all conditions, there is a make-up air duct, which draws atmospheric air into the tail-gas line, upstream of the Axi-Shear unit. This dilutes the stack gases discharged from the unit.

Figure 3-6 Axi-Shear Scrubber Unit



A recirculating water flow is maintained within the Axi-Shear sump via recirculation pump P–331. As incoming chlorine and nitric oxide gas is scrubbed from the gas streams the resultant acid product is neutralized through the addition of sodium hydroxide solution. Control of pH is accomplished through a pH analyzer and controller located on the recirculating loop. The analyzer/controller adjusts the speed of the sodium hydroxide metering pump (P-330) to maintain a preset pH within the acceptable discharge limits established by the local POTW. An independent pH analyzer is located on the discharge piping of the scrubber system equalization drum and measures and records the actual pH of the discharge to the local POTW. The pH analyzer is equipped with a low and a high pH alarm which results in the complete shutdown of the CerOx unit should either be activated.

3.4 Utility and Support Systems

3.4.1 Instrument Air

An instrument air dryer, XX–420, is provided to supply dry air to instruments requiring an air source within the CerOx System 2. The instrument air dryer system is equipped with a 2.5-gallon receiver to maintain a working volume of instrument air for system operation. Instrument air is supplied at 80 psi and pressure monitored with a pressure element. Loss of instrument air pressure below 70 psi results in a shutdown of the system. The source of compressed air is from the Applied Research Facilities compressor system.

3.4.2 Cooling Tower

A packed cooling tower system, XX-410, is provided for the purpose of supplying cooling water for temperature control within CerOx System 2. The cooling tower is supplied as a purchased stand-alone unit which is instrumented and controlled to provide a constant flow of cooling water to the system via recirculation pump, P-410, for removal of the generated heat load and its rejection to atmosphere. Loss of the cooling water system will result in the inability to reject heat from the operation and thus will result in a shutdown of CerOx System 2.

The cooling tower is equipped with a forced draft fan, which circulates atmospheric air through the packing counter current to the water flow to cool the incoming liquid flow. Freeze protection is provided within the cooling tower sump via a thermostatically controlled heater, which is activated if the sump liquid contents fall below 40 °F. External lines are also heat traced and insulated for freeze protection since the unit is mounted outside.

3.4.3 Nitric Acid Supply

Nitric acid must be added to Catholyte Tank (TK-110) to compensate for acid losses from un-recovered NOx and from vent losses out of the anolyte and reactor tanks. It is also necessary to maintain concentration of nitric acid at the set point to minimize the evolution of hydrogen gas from the catholyte solution. Catholyte acid strength is monitored by a conductivity sensor on the catholyte circuit and maintained within prescribed concentrations by subsequent on/off control of the nitric acid addition pump, P-401. Bulk nitric acid (36° to 42° Baumé) is provided in 55-gallon drums. For the LEST, the nitric acid drum was placed on a drum scale to facilitate the calculation of mass flow to the system.

3.4.4 Sodium Hydroxide Supply

Sodium hydroxide (25 to 30 - wt%) is utilized to neutralize acid aqueous solutions generated by the scrubbing of acid gases from the CerOx System 2 process. The bulk 55-gallon supply drum, DR-402, supplies the Axi-Shear unit's Caustic Metering Pump, P-330 (PTFE wetted parts) not shown. For the

LEST, the sodium hydroxide drum was gauged for calculation of consumption rates.

3.4.5 Wastewater Collection Tank

CerOx subcontracted with Baker Tank to provide a 4000-gallon wastewater collection tank for the LEST. The normal discharge of scrubber effluent was routed to the temporary wastewater collection tank during all validation tests. The wastewater collection tank was piped to the POTW collection header with a drain valve, which remained in the closed position during all validation testing.

Figure 3-7 CerOx System 2 - Process Flow Diagram (Configuration 1)

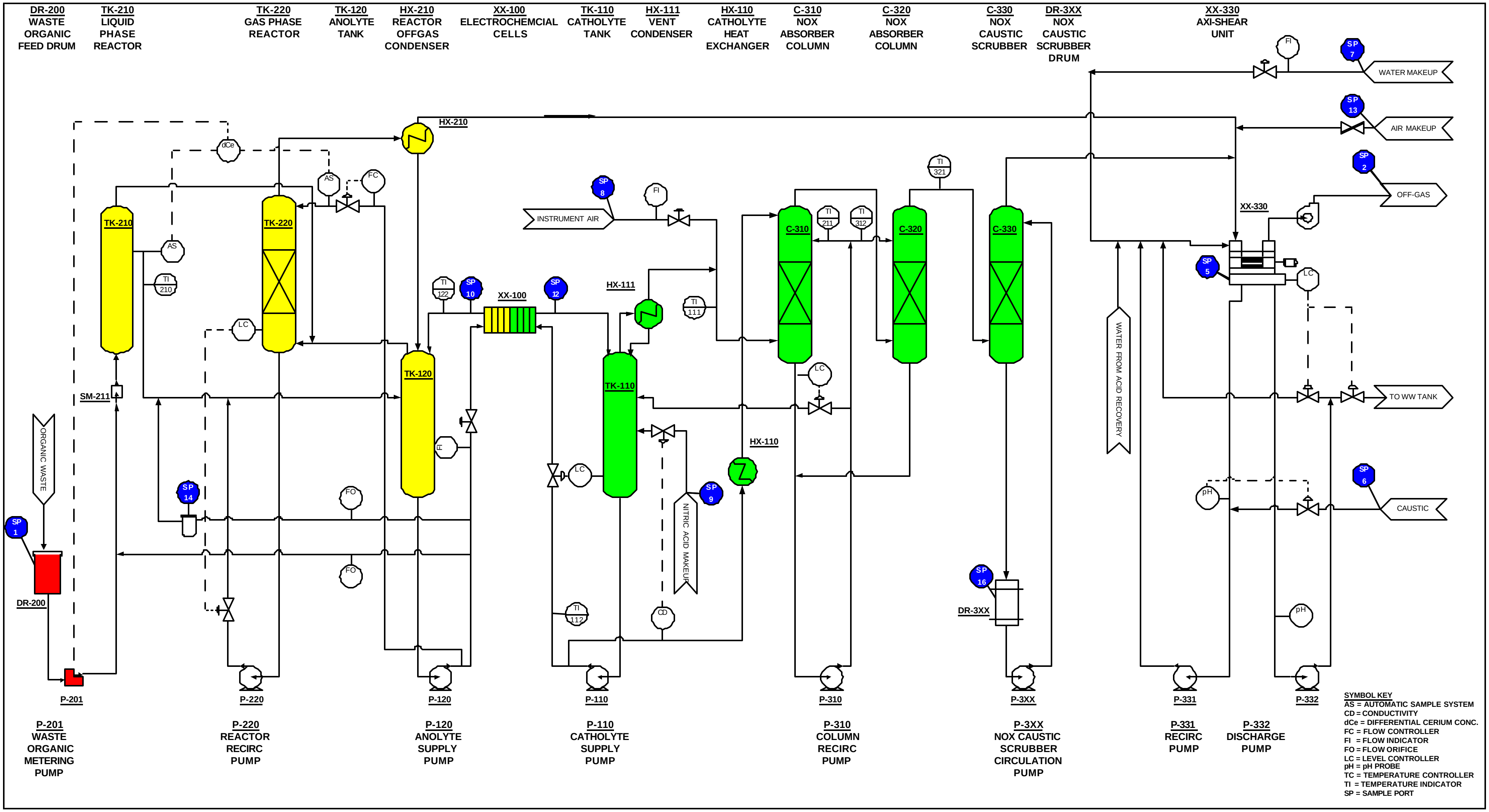
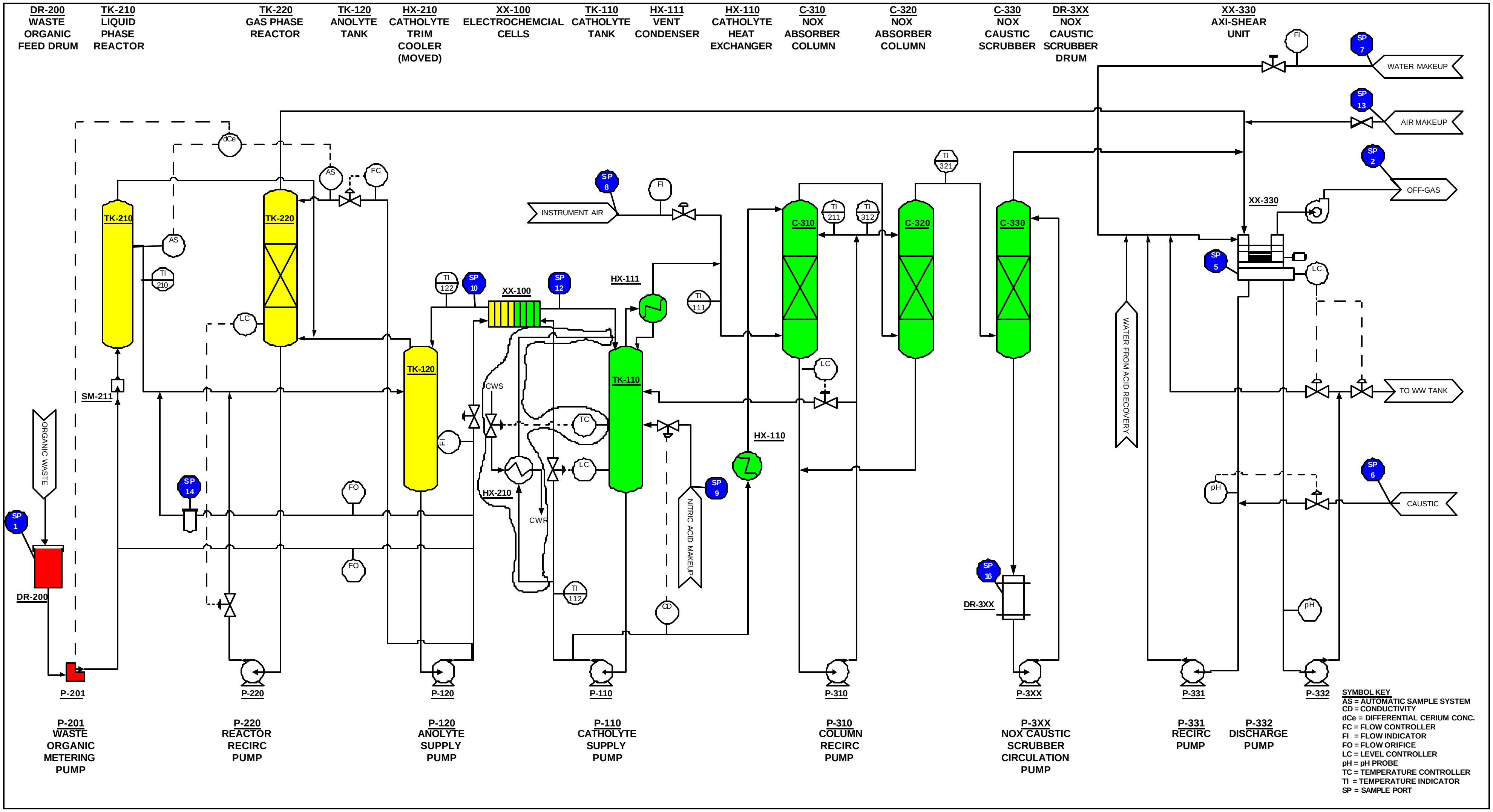


Figure 3-8 CerOx System 2 - Process Flow Diagram (Configuration 2)



4. TEST DESCRIPTION

This section presents descriptions of the CerOx System 2 LEST conducted during May and June of 2001. The test descriptions include a discussion of the neutralent simulant feeds, descriptions of each test run, and the sampling and analyses conducted.

4.1 Simulants

Two NSCMP neutralent simulants were tested during the six test runs. Both feed streams simulated Monoethanolamine (MEA)-based Munitions Management Device (MMD) neutralents.[7] The composition of each simulant and comparison with NSCMP neutralent are shown in Table 4-1.

Table 4-1 Neutralent Simulant Compositions

	NSCMP NEUTRALENT					NEUTRALENT SIMULANT					
Agent Neutralents	Major Components	Chemical Formula	Wt% in neutralent[1]	Comp MW	Molar flowrate[2] kmol/h	Equivalent component in Simulant	Chemical Formula	Molar flowrate[3] in kmol/h	Simulant MW	Calculated Mass flowrate in kg/h	Wt% in Simulant
HD Neutralent in MEA	MEA	C_2H_7NO	78	61	1.28	MEA	C_2H_7NO	1.28	61	78.00	83.0
	Water	H_2O	9.5	18	0.53	Water	H_2O	0.53	18	9.50	10.1
	MEA HCl	$C_2H_8ON\mathbf{Cl}$	7.25	97	0.07	Dichloroethane	$C_2H_4\mathbf{Cl_2}$	0.04	99	3.70	3.9
	HETM	$C_6H_{13}NO\mathbf{S}$	5.25	147	0.04	Dimethylsulfoxide	$C_2H_6O\mathbf{S}$	0.04	78	2.79	3.0
	TOTAL		100							93.99	100.0
GB Neutralent in MEA	MEA	C_2H_7NO	38	61	0.62	MEA	C_2H_7NO	0.72	61	43.69	39.9
	Water	H_2O	50	18	2.78	Water	H_2O	3.19	18	57.49	52.4
	MEA IMP	$C_4H_{10}O_3\mathbf{P}$	5	137	0.04	DMMP	$C_3H_9O_3\mathbf{P}$	0.05	124	6.61	6.0
	MEA HF	$C_2H_8ON\mathbf{F}$	4	81	0.05	Ammonium Fluoride	$NH4\mathbf{F}$	0.05	37	1.83	1.7
	GB MEA	$C_6H_{15}NO_3\mathbf{P}$	3	181	0.02						
	TOTAL		100							109.63	100.0

Assumptions

1) Percentages taken from MMD-1 RD&D, RCRA Permit Application, Attachment 4, Appendix A, page 6. An average value within the quoted range was chosen.

2) Assume total flowrate of 100 kg/h for calculation purposes.

3) Molar flow rates of simulant compounds are calculated based on the number of moles of the critical hetero atom (bold font) and compounds in the neutralent streams.

4.2 Test Run Descriptions

The Limited Engineering Scale Testing of the CerOx Process consisted of six validation test runs at the CerOx System 2 Unit installed at the University of Nevada at Reno's facilities in Reno, Nevada between May 23 to June 5, 2001. The CerOx test plan proposed two 8 hr and one 24 hr test per neutralent simulant test campaigns (HD and GB neutralent simulant campaigns). In addition to the six validation runs, CerOx conducted Work-Up runs before each of the neutralent simulant test campaigns to check operability and prepare for validation tests. Analytical data were not collected during the Work-Up runs.

The test plan specified sampling and analysis of liquid, solid, and gaseous streams from all six test runs. Stone & Webster subcontracted the sampling services to TRC Environmental Corporation. CerOx Corporation performed the analyses of the electrolyte solutions to establish their gross compositions, i.e., the cerium and nitric acid concentrations of the electrolytes.

Table 4-2 and Table 4-3 show the results of the HD and GB neutralent simulant validation test runs respectively.

Table 4-2 HD Neutralent Simulant Test Summaries

Test	Units	HD-2	HD-3	HD-4
Date of Test - 2001		May 23	May 30	May 24-25
Run Time[1]	hrs	8	8	24
Off-Line Time[2]	hrs	0.58	0	1.5
Neutralent Simulant Feed				
Total Mass	kg	9.74	12.36	34.98
Average Flow	kg/hr	1.22	1.55	1.46
Cell Current	amps	500-450	450	450
Electrical Energy	kW-hr	241	234	712
Discharge Water				
Flow Rate	gpm	1.6	1	1.6
Total Flow	gal	768	480	2304
pH		9.3	8.4	9.3
Make-up Acid[3]	kg	NA	49.5	149.5
Caustic Solution Consumption[4]				
NOx Scrubber	gal	8+initial	40	52
Axi-Sheer	gal	6.9	6.9	20.6
Performance				
Energy/Feed	kW-hr/kg	24.7	18.9	20.4

Notes:
1. Run time is accumulation of testing with feed.
2. Off-line time is the accumulation of time without feed during scheduled
3. Make-up acid is 42° Baume HNO_3.
4. Caustic is a 25 wt% NaOH solution.

Table 4-3 GB Neutralent Simulant Test Summaries

Test	Units	GB-2	GB-3	GB-4
Date of Test - 2001		June 4	June 5	June 1-2
Run Time[1]	hrs	8	8	24
Off-Line Time[2]	hrs	0	0	0
Neutralent Simulant Feed				
Total Mass	kg	20.9	19.2	57.6
Average Flow	kg/hr	2.61	2.40	2.40
Cell Current	amps	450	450	450
Electrical Energy	kW-hr	286	260	733
Discharge Water				
Flow Rate	gpm	0.6	0.6	0.6
Total Flow	gal	288	288	864
pH		7.6	7.5	7.6
Make-up Acid[3]	kg	50	NA	142
Caustic Solution Consumption[4]				
NOx Scrubber	gal	40	40	85
Axi-Sheer	gal	6.9	6.9	20.6
Performance				
Energy/Feed	kW-hr/kg	13.7	13.5	12.7

Notes:
1. Run time is accumulation of testing with feed.
2. Off-line time is the accumulation of time without feed during schedulec
3. Make-up acid is 42° Baume HNO_3.
4. Caustic is a 25 wt% NaOH solution.

Prior to the beginning of the tests, CerOx installed new electrolytic cells (reflecting the latest design) and a new single cartridge anolyte filter. After the equipment installations, the unit was charged with 75 gallons of fresh catholyte (3.5 M nitric acid in water) and 110 gallons of fresh anolyte (nominal 1.5M cerium nitrate and 3.5M nitric acid).

CerOx also prepared the neutralent simulant solutions. All of the solutions were mixed on a mass basis in clean drums. The components were added to the drum, which was set on a drum scale. Mixing was accomplished by recirculating the drum contents using a diaphragm pump.

Initially, the unit has no Ce^{+4} concentration in the anolyte solution. At 1500h on May 22, 2001, CerOx turned on the unit (circulating fluids and electric current to cells) to build the concentration of Ce^{+4} to about 1M in the anolyte to prepare for the work-up run to follow.

4.2.1 Work-up Test Run HD-1

On May 23, 2001 at 1100h, the CerOx System 2 was brought online for the work-up run. CerOx initially estimated a HD neutralent simulant feed rate to maintain a concentration of Ce^{+4} in the anolyte. The initial feed rate was set at approximately 1.4 kg/hr with cell current set to ramp up to 500 amps. CerOx began taking data on the Ce^{+4} concentration in the anolyte. At 1145 hrs, UNR's operators accidentally caused the run to abort due to keyboard error on the control console (the keyboard was moved for data collection and the abort key was accidentally engaged). The unit was immediately restarted. At 1315h, the current to the electrolytic cells was reduced due to excess heat generation in the catholyte and anolyte systems. CerOx concluded that the feed rate to the unit was too high and the associated heat of reaction was causing excessive heat. The feed rate was subsequently reduced to approximately 1.3 kg/hr and the unit was prepared for the first validation run HD-2 described in the next section.

4.2.2 Test Run HD-2

Test Run HD-2 was an 8-hour validation run on May 23, 2001. Figure 4-1 shows the raw Continuous Emission Monitoring (CEM) data while Figure 4-2 shows some of the temperature profiles of process fluids from the CerOx Supervisory Control and Data Acquisition (SCADA) system.

The start-of-run (SOR) was at 1400h and had an initial flow rate set at 1.28 kg/hr of the HD neutralent simulant. CerOx set the initial cell current at 500 amps. Make-up water to the Axi-Shear unit was set at 1.6 gpm. CerOx calculated the flow rate of make-up water to provide adequate water to the Axi-Shear Scrubber and meet the local permit requirements for total chlorides. All of the scrubber effluent from the system was collected in a 4000-gallon tank and analyzed for TOC and chloride prior to disposal to the POTW.

TRC logged and recorded data measured in the stack gases from the unit using their Continuous Emissions Monitoring (CEM) equipment. The Total Hydrocarbon Analyzer (THC) was off-line most of the test due to a malfunctioning analyzer. A summary of the stack data is shown in Figure 4-1. TRC also pulled the initial process samples for laboratory analyses.

At 1450h, the DC power supply registered a high temperature condition, which initiated an automatic shutdown of the CerOx Unit. The most probable cause of the high temperature condition was cardboard boxes blocking the air inlet vents around the DC power supply that prevented adequate cooling. During the shutdown, TRC temporarily stopped their process sampling activities but continued monitoring the stack gases using the CEM equipment since the unit still produces stack gases from the operating scrubbing systems.

The DC power supply was restored at 1515h and the HD neutralent simulant feed was recommenced at 1520h along with the TRC process sampling activities. At 1630h, CerOx reduced the cell current to 450 amps to help control the heat accumulation in the anolyte and catholyte systems. The anolyte and catholyte temperatures were trending upwards to a point where there was an increased risk of boiling the nitric acid based anolyte and catholyte solutions.

At 1820h, TRC reported that NOx and SO_2 levels in the stack gas were increasing. This suggested that the NOx Caustic Scrubber had lost some of its original scrubbing efficiency. Since the scrubbing solution is not continuously replenished with fresh caustic solution, 8 gallons of spent scrubbing solution was removed from the NOx Caustic Scrubber Drum and replaced with 4 gallons of fresh caustic solution (25%). The immediate and dramatic response can be seen in Figure 4-1.

Slightly after 2000h, the N_2O analyzer began to malfunction for no explained reason. Data gathered after 2000h is erroneous and will not be used for data analyses.

At 2100h, the THC analyzer was started up. After calibrations, the analyzer became operational at 2219h.

At 2230h, the 8-hr validation test was complete with a total 9.74 kg of feed treated during the test, which resulted in an average feed rate of 1.22 kg/hr. During the test the anolyte was periodically measured for Ce^{+4} concentration and ranged from 0.84 to 0.89M.

Following the run, the DC power to the unit was turned off and organic feed was continued to reduce the concentration of Ce^{+4} in the anolyte. This is normal practice with the purpose to leave the unit in a desirable start-up condition (Ce^{+4} concentration approximately 0.5M). During the start-up sequence, the unit is warmed up by turning on the power to the cells while the anolyte and catholyte solutions are circulating. CerOx stated that during the warm-up phase, it is desirable to build Ce^{+4} concentration rather than electrolyze water, a parasitic process that wastes electrical energy (see Section 5.2).

At 0840h on May 24, 2001, the anolyte filter was removed along with the contents of the anolyte filter housing. Anolyte filter solids were extremely fine and were a greenish brown color. The quantity of solids was undetermined do to the complications associated with supplying filter samples to multiple laboratories for analysis and the fact that so little solids were generated. CerOx estimated the total solids generated at less than a couple of grams.

Figure 4-1 CEM Stack Gas Data (Raw) - HD-2

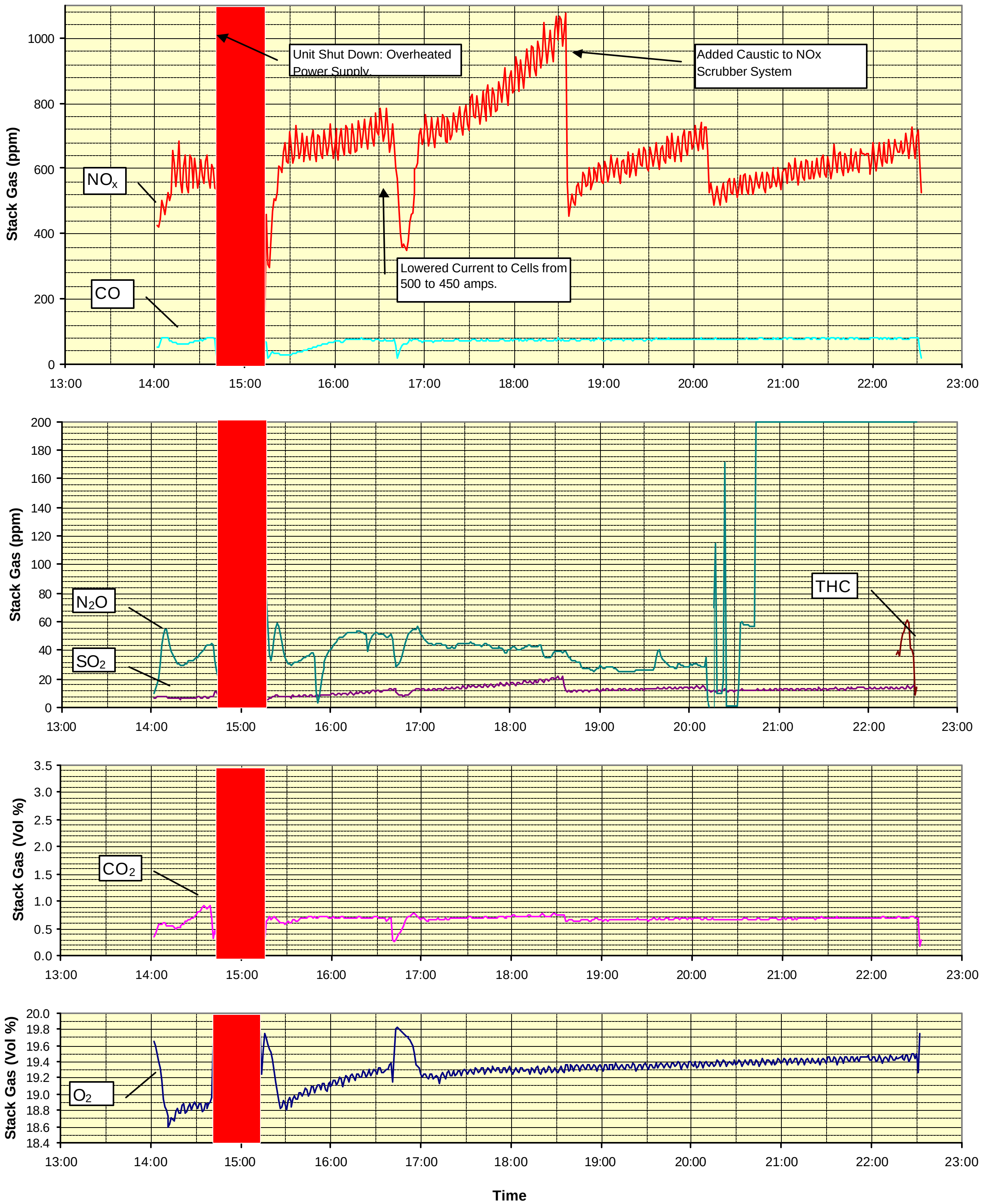
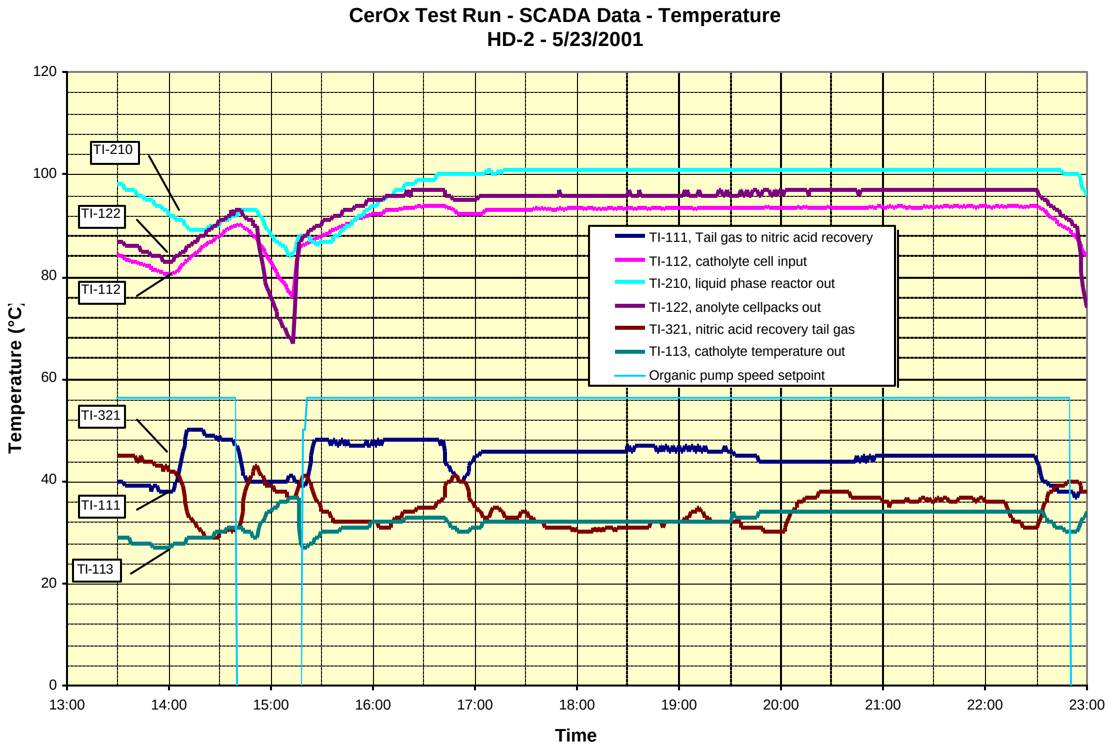


Figure 4-2 Process Temperature Monitoring Data - HD-2



4.2.3 Test Run HD-4

Test Run HD-4 was run on May 24-25, 2001 with a scheduled run time of 24 hours. This test was performed before the HD-3 test due to scheduling constraints afforded by the Memorial Holiday weekend and personnel availability. Figure 4-3 shows the raw CEM data while Figure 4-4 shows some of the temperature profiles of process fluids from the CerOx SCADA system.

The CerOx unit was put in start-up mode at 0800h, which initiated the unit warm-up and generation of Ce^{+4} concentration. The NOx Scrubber Solution Drum was drained and charged with 40 gallons of 25% caustic solution. The SOR of the validation test was initiated at 0932h and had an initial flow rate set at 1.2 kg/hr of the HD neutralent simulant. CerOx set the initial cell current at 450 amps. TRC logged and recorded data measured in the stack gases from the unit using their CEM equipment. A summary of the stack data is shown in Figure 4-3.

As illustrated in Figure 4-4, the temperatures of the anolyte and catholyte systems steadily rose during the first couple of hours of the test. In fact, the temperatures rose to a point where the electrolytes in the cells were boiling (1315h). This prompted CerOx to switch from automatic to manual mode and switch off the DC current to the cells. While still circulating the anolyte and catholyte solutions, the catholyte pump started to cavitate (1335h) at which point the catholyte and anolyte pumps were switched off. 5 minutes later, the catholyte pump was restarted which was followed by restarting the anolyte pump. After the pumps reached full flow the insulation was removed from the catholyte tank to increase the heat loss from the vessel. At 1354h, the unit was restarted in auto mode with the DC current set at 100 amps. During the normal start-up sequence, the organic feed pump started at 1400h which was immediately followed by a high level alarm in the Gas Phase Reactor which automatically initiated a shutdown. The control system was set in manual and the reactor recirculation pump was turned on for a short burst to reduce the liquid level in the Gas Phase Reactor. The unit was restarted in automatic with the cell current at 200 amps and organic feed resumed at 1410h. This was followed by a steady build of current to the cells with the final set point at 450 amps.

At 1549h, a level sensor fault (loss of signal) which measures the level in the NOx Absorber Columns was detected by the system and caused an automatic shutdown. CerOx removed the cover from the level instrument and regained control of the signal. Organic feed was resumed at 1605h. At 0200 (May 25, 2001) 9 gallons of fresh 25% caustic was added to the NOx Caustic Scrubber Drum due to increasing levels of NOx in the stack gases.

At 0845h, CerOx noticed that the temperature of the outlet of the Liquid Phase Reactor was decreasing. Upon investigation, it was discovered that the suction tube in the organic feed tank was not all the way to the bottom. When the level in the organic feed tank fell below the bottom of the suction tube, the feed rate of organic solution was effectively stopped. The problem was fixed by extending the suction tube to the bottom of the tank and organic feed was resumed at 0900h.

0930h was marked by the addition of 3 gallons of 25% caustic solution to the NOx Caustic Scrubber Drum to combat the increasing NOx concentration being measured in the stack gases.

1030h marked the EOR for the HD-4 validation test with an accumulated test duration of 24 hours. A total of 34.98 kg of feed was treated during the test, which resulted in an average feed rate of 1.46 kg/hr (nominal cell current of 450 amps). During the test the anolyte was periodically measured for Ce^{+4} concentration and ranged from 0.83 to 1.06M.

Following the run, the DC power to the unit was turned off and organic feed was continued to reduce the concentration of Ce^{+4} in the anolyte.

Anolyte filter solids were extremely fine and were a greenish brown color. The quantity of solids was undetermined do to the complications associated with supplying filter samples to multiple laboratories for analysis and the fact that so little solids were generated. CerOx estimated the total solids generated at less than a couple of grams.

Figure 4-3 CEM Stack Gas Data (Raw) - HD-4

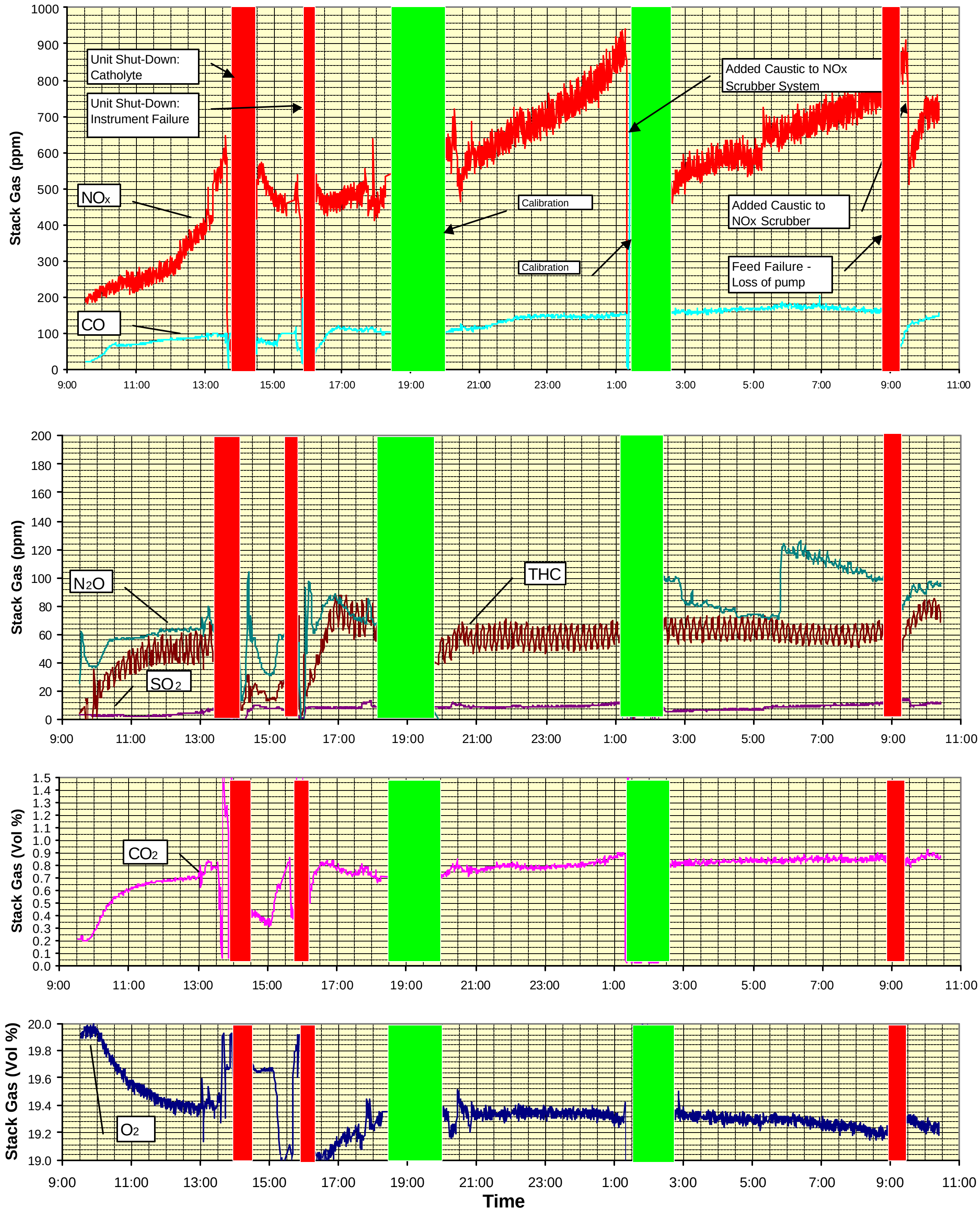
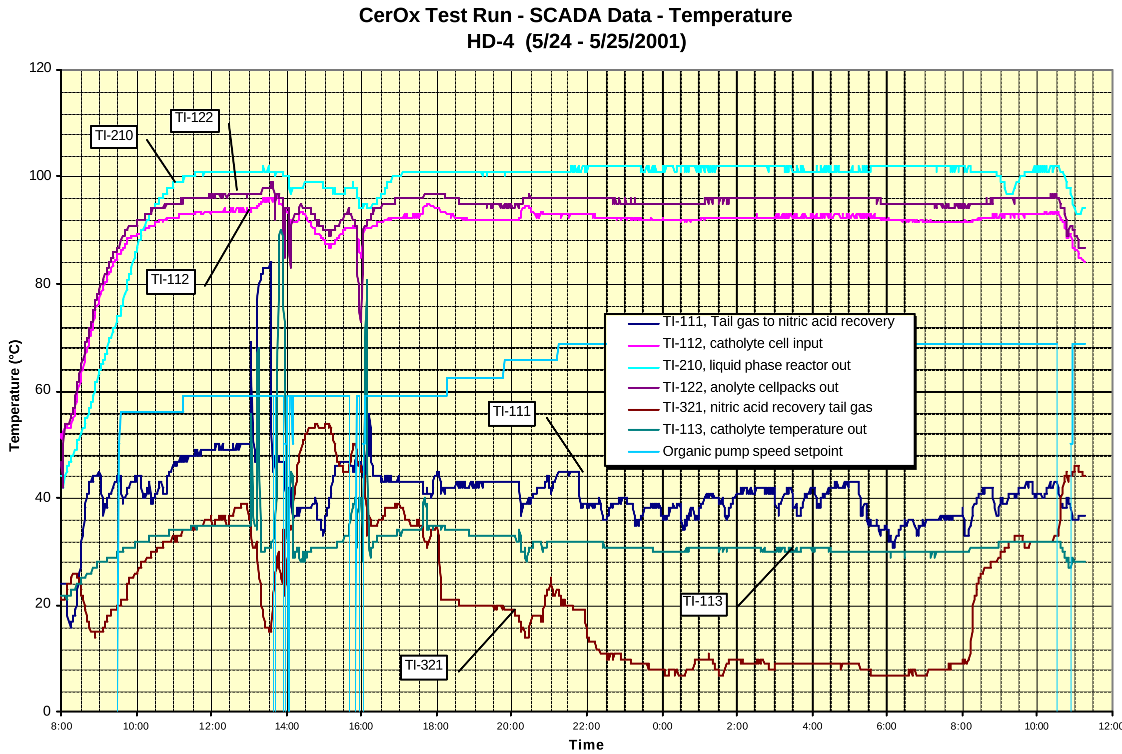


Figure 4-4 Process Temperature Monitoring Data - HD-4



4.2.4 Test Run HD-3

Prior to the start of the HD-3 run, CerOx reconfigured the heat exchanger arrangement in order to provide a trim cooler on the catholyte circulation loop (see the new position of HX-210 in Figure 3-8). This was accomplished by re-piping the Reactor Offgas Condenser (HX-210), which was not utilized in the previous tests because it has little impact on the process, to cool a slipstream of catholyte solution downstream of the Catholyte Supply Pump (P-110). A control valve, reset by the catholyte tank (TK-110) temperature, was installed on the cooling water supply line. This modification enabled the unit to have additional heat exchanger area available to help cool the catholyte solution, which is the main mechanism for heat transfer out of the system.

The two previous runs had nearly filled the 4000-gallon wastewater storage tank. Samples were taken from the tank for TOC and chloride analysis. Laboratory results from Alpha Analytical reported a TOC level of 8.5 mg/L in the wastewater tank sample. The chloride content was measured by TRC at 52.5 ppm using a Hach Quantab. The site-operating permit allowed for 100 ppm TOC and 110 ppm Chloride in the scrubber effluent discharge to the POTW. The wastewater tank was subsequently drained to the POTW.

Test Run HD-3 was an 8-hour validation run on May 30, 2001. Figure 4-5 shows the raw CEM data while Figure 4-6 shows some of the temperature profiles of process fluids from the CerOx SCADA system. The SOR was at 1000h and had an initial flow rate set at 1.6 kg/hr of the HD neutralent simulant.

CerOx set the initial cell current at 450 amps. The make-up water flow rate to the Axi-Shear scrubber system was reduced from previous runs, which averaged 1.6 gpm, to a new value of approximately 1 gpm. The new make-up water flow rate is closer to the normal operating requirements for the scrubbing system (normally 0.5 to 0.6 gpm). The additional flow of make-up water from the previous runs was calculated to meet permit requirements for chloride. The high make-up water flow rate would not be required in subsequent runs since the majority of the testing to follow would be with non-chlorine containing feeds.

TRC logged and recorded data measured in the stack gases from the unit using their CEM equipment. A summary of the stack data is shown in Figure 4-5. TRC also pulled the initial, intermediate, and final process samples for laboratory analyses.

At 1420h, approximately 40 gallons of scrubbing solution was drained from the NOx Caustic Scrubber Drum. 40 gallons of fresh 25% caustic solution was then charged to the drum. The immediate and dramatic response can be seen in Figure 4-5.

At 1800h, the 8-hr validation test was complete with a total of 12.36 kg of feed treated during the test, which resulted in an average feed rate of 1.55 kg/hr. During the test the anolyte was periodically measured for Ce^{+4} concentration and ranged from 0.84 to 0.73M. No unscheduled shutdowns occurred during the run.

Following the run, the normal shutdown sequence was followed.

Anolyte filter solids were extremely fine and were a greenish brown color. The quantity of solids was undetermined do to the complications associated with supplying filter samples to multiple laboratories for analysis and the fact that so little solids were generated. CerOx estimated the total solids generated at less than a couple of grams.

Figure 4-5 CEM Stack Gas Data (Raw) - HD-3

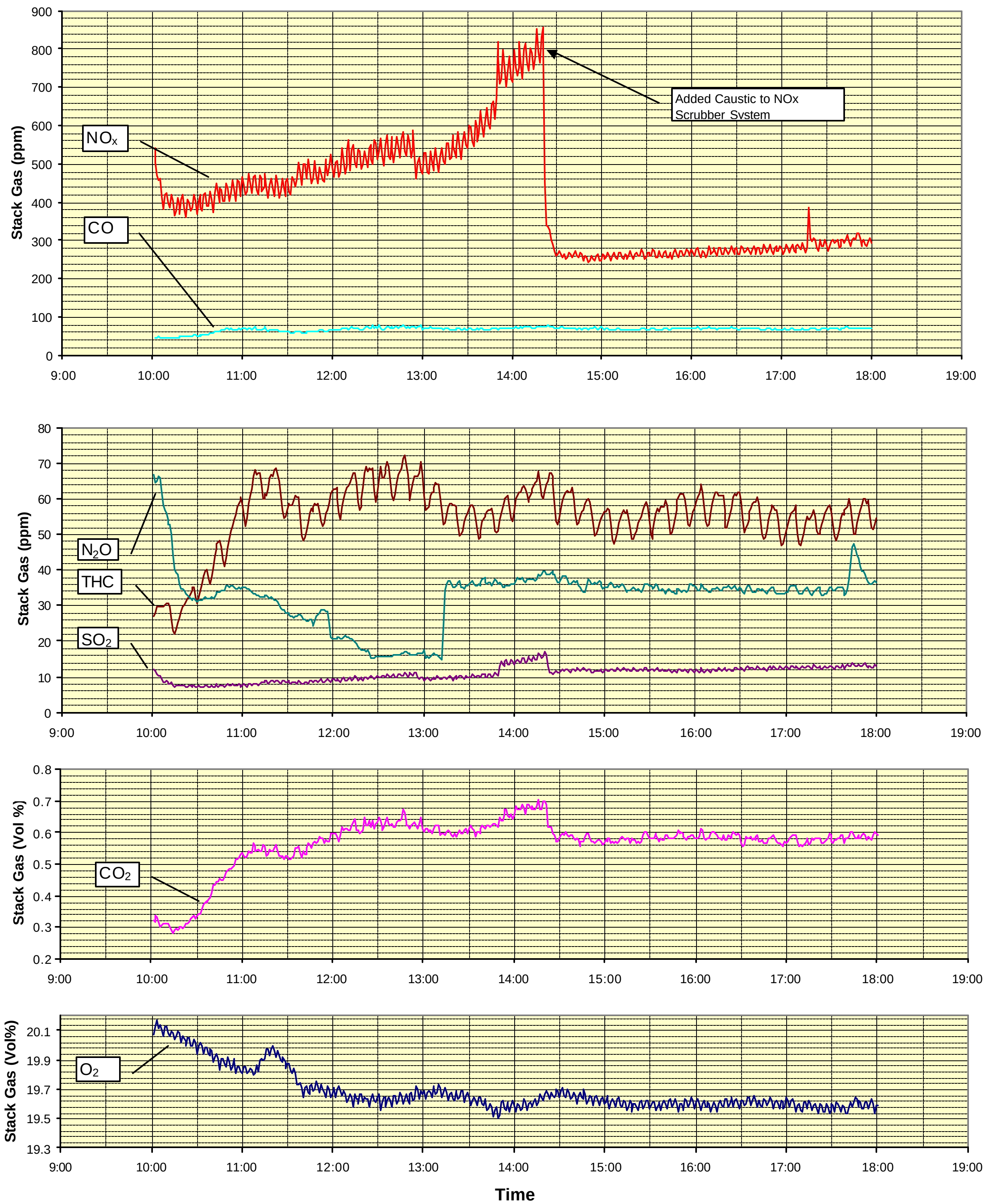
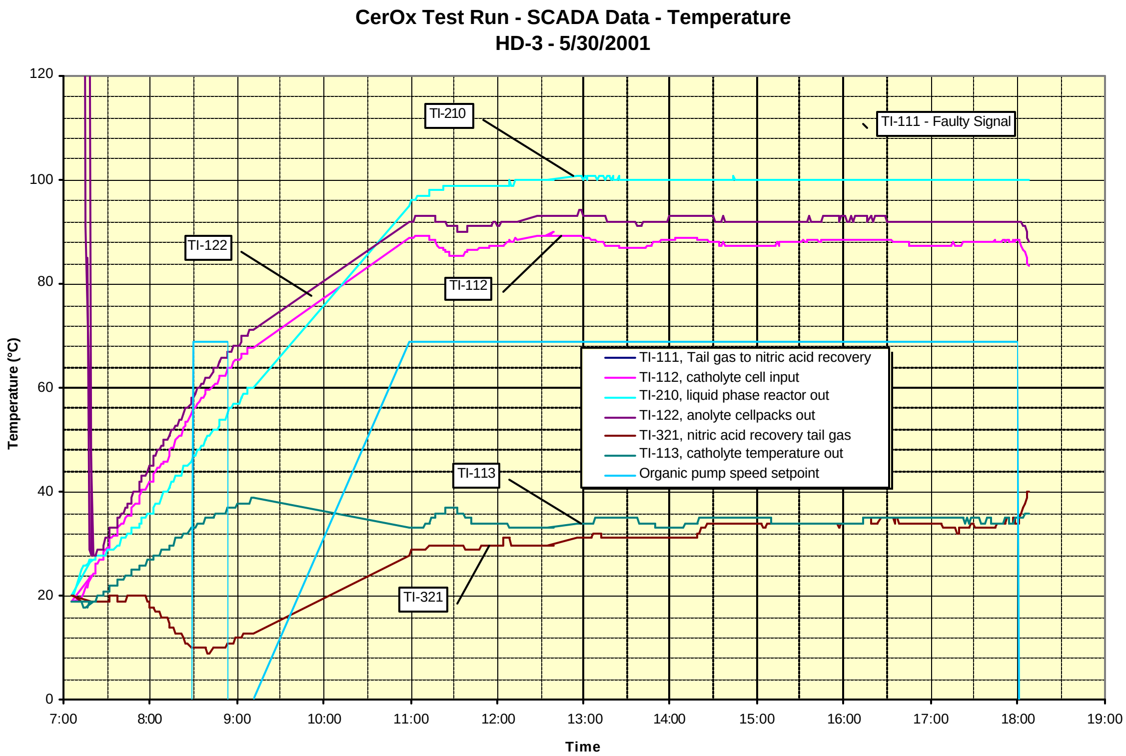


Figure 4-6 Process Temperature Monitoring Data - HD-3



4.2.5 Work-up Test Run GB-1

After the HD neutralent simulant test campaign and according to the test plan, CerOx drained the System 2 of anolyte and catholyte solutions (May 31, 2001). Fresh anolyte and catholyte were then charged to the system in preparation for the GB neutralent simulant test campaign. At 1515 (May 31, 2001) the unit was turned on and the automated Ce^{+4} build cycle was initiated (approximately 0.5M Ce^{+4} generated per hour). Unit was subsequently shut down for the evening in preparation for the 24 hour GB test schedule to begin on June 1, 2001. GB neutralent simulant was not fed to the unit during the work-up run.

4.2.6 Test Run GB-4

Test Run GB-4 was a 24-hour validation run on June 1 and June 2, 2001. This test run was scheduled before GB-2 and GB-3 to accommodate personnel availability for the 24-hour duration. Figure 4-7 shows the raw CEM data while Figure 4-8 shows some of the temperature profiles of process fluids from the CerOx SCADA system. The SOR was at 09:00h (June 1, 2001) and had an initial flow rate set at approximately 2.5 kg/hr of the GB neutralent simulant. The increased flow rate of organic feed was due to the fact that the GB neutralent simulant contains about half the organic content as the HD neutralent simulant. CerOx set the initial cell current at 450 amps. The make-up water flow rate to the Axi-Shear scrubber system was set at approximately

0.6 gpm which is consistent with normal operating requirements for the scrubbing system (normally 0.5 to 0.6 gpm).

TRC logged and recorded data measured in the stack gases from the unit using their CEM equipment. A summary of the stack data is shown in Figure 4-7. TRC also pulled the initial, intermediate, and final process samples for laboratory analyses.

At 2310h, scrubbing solution from the NOx Caustic Scrubber Drum was drained and 45 gallons of fresh 25% caustic solution was charged to the drum to combat increasing NOx concentrations in the stack gases. The immediate and dramatic response in the NOx stack gas concentrations can be seen in Figure 4-8.

At 0800h (June 2, 2001), a leak developed in the flange where the catholyte return enters the Catholyte Tank. The flange bolts were tightened without apparent effect on the drip rate.

At 0900h (June 2, 2001) the 24-hr validation test was complete with a total of 57.6 kg of feed treated during the test, which resulted in an average feed rate of 2.4 kg/hr. During the test the anolyte was periodically measured for Ce^{+4} concentration and ranged from 0.75 to 0.64M. No unscheduled shutdowns occurred during the run.

Following the run, the normal shutdown sequence was followed.

Anolyte filter solids were extremely fine and were a greenish brown color. The quantity of solids was undetermined do to the complications associated with supplying filter samples to multiple laboratories for analysis and the fact that so little solids were generated. CerOx estimated the total solids generated at less than a couple of grams.

Figure 4-7 CEM Stack Gas Data (Raw) - GB-4

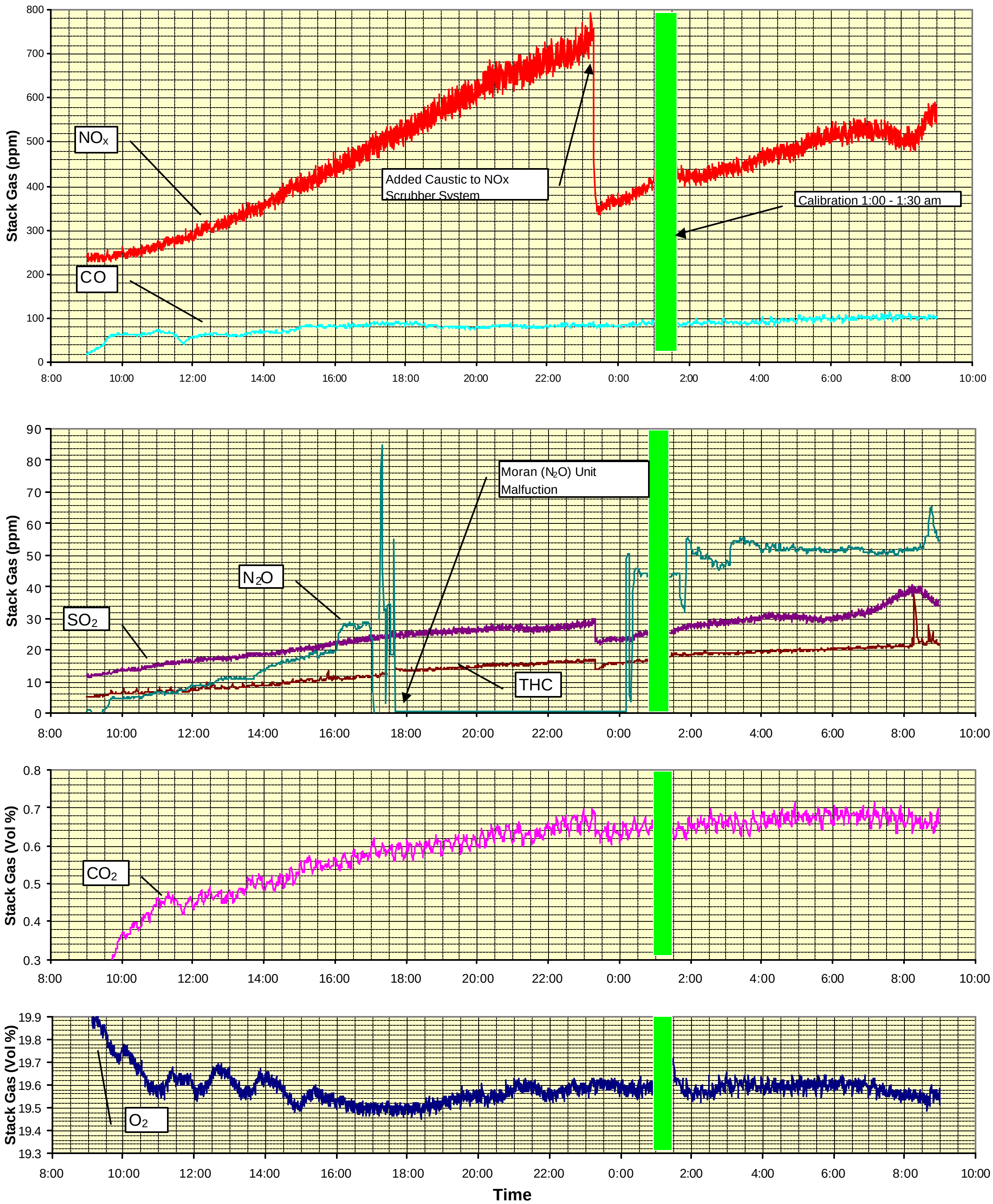
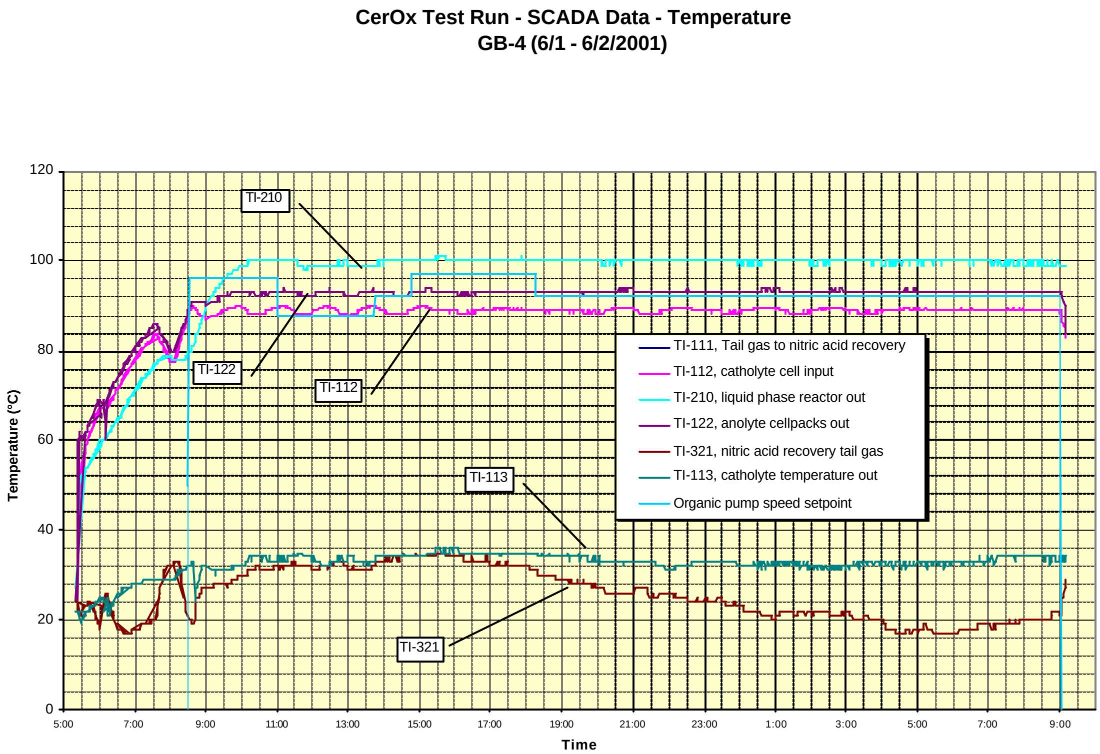


Figure 4-8 Process Temperature Monitoring Data - GB-4



4.2.7 Test Run GB-2

Prior to the GB-2 test run, CerOx repaired the leaking flange discovered in the GB-4 test run. The repair to the leaking flange included a gasket change and replacement of the stainless steel spoolpiece with a PVDF spoolpiece.

Test Run GB-2 was an 8-hour validation run on June 4, 2001. Figure 4-9 shows the raw CEM data while Figure 4-10 shows some of the temperature profiles of process fluids from the CerOx SCADA system. The SOR was at 11:00h (June 1, 2001) and had an initial flow rate set at approximately 2.5 kg/hr of the GB neutralent simulant. CerOx set the initial cell current at 450 amps. The make-up water flow rate to the Axi-Shear scrubber system was set at approximately 0.6 gpm.

TRC logged and recorded data measured in the stack gases from the unit using their CEM equipment. A summary of the stack data is shown in Figure 4-9. TRC also pulled the initial, intermediate, and final process samples for laboratory analyses.

At 1900h, the 8-hr validation test was complete with a total of 20.9 kg of feed treated during the test, which resulted in an average feed rate of 2.61 kg/hr. During the test the anolyte was periodically measured for Ce^{+4} concentration and ranged from 0.71 to 0.64M. Figure 4-10 shows the operating temperatures during the test run. No unscheduled shutdowns occurred during the run.

Following the run, the normal shutdown sequence was followed.

Anolyte filter solids were extremely fine and were a greenish brown color. The quantity of solids was undetermined do to the complications associated with supplying filter samples to multiple laboratories for analysis and the fact that so little solids were generated. CerOx estimated the total solids generated at less than a couple of grams.

Figure 4-9 CEM Stack Gas Data (Raw) - GB-2

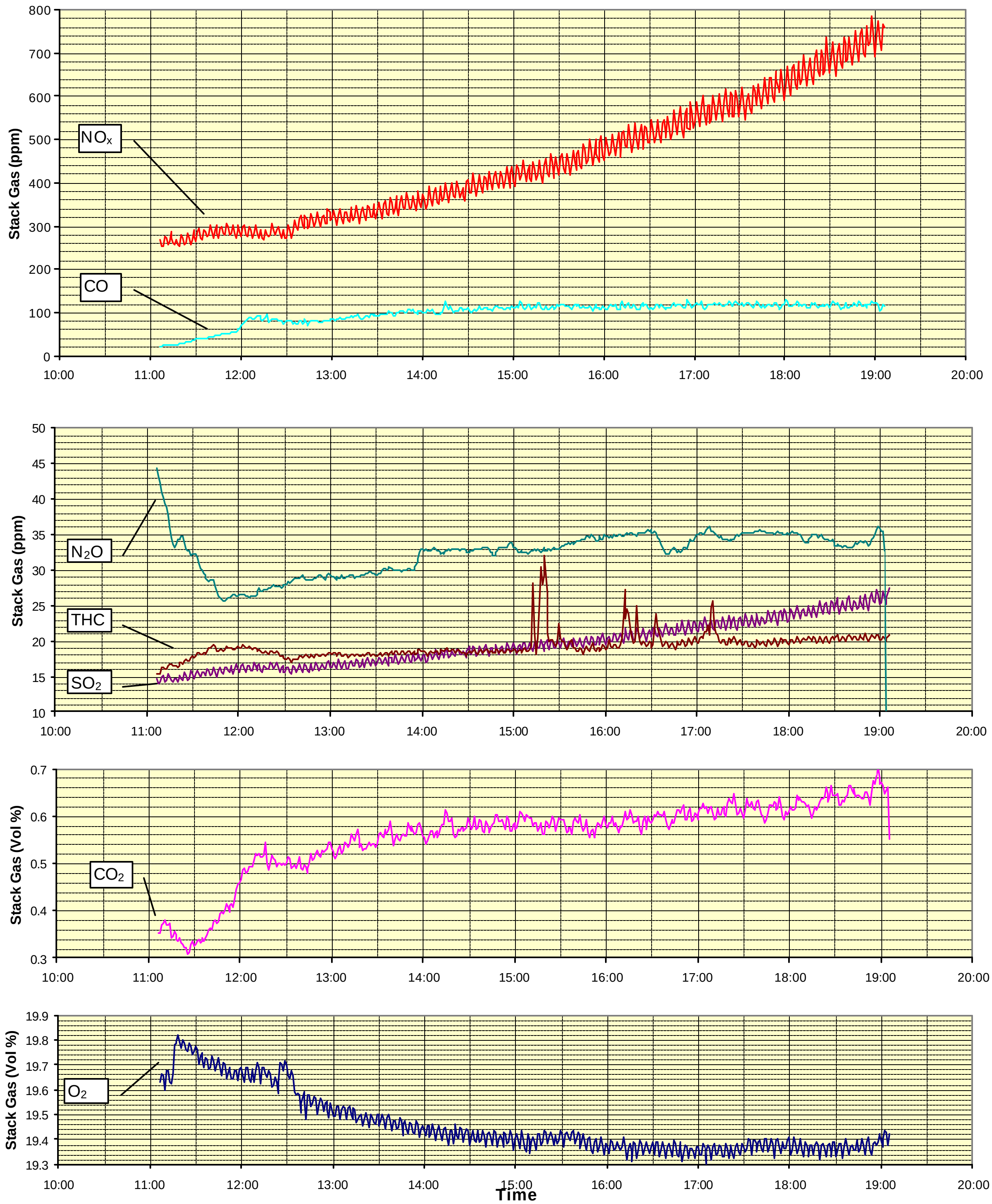
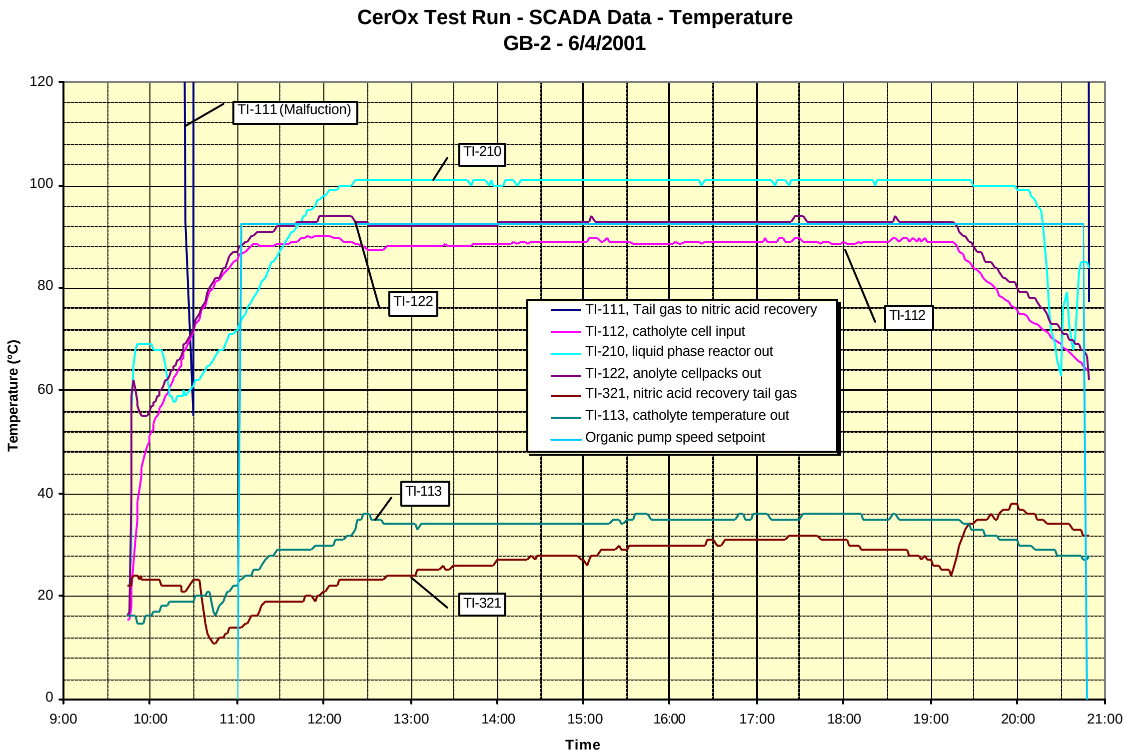


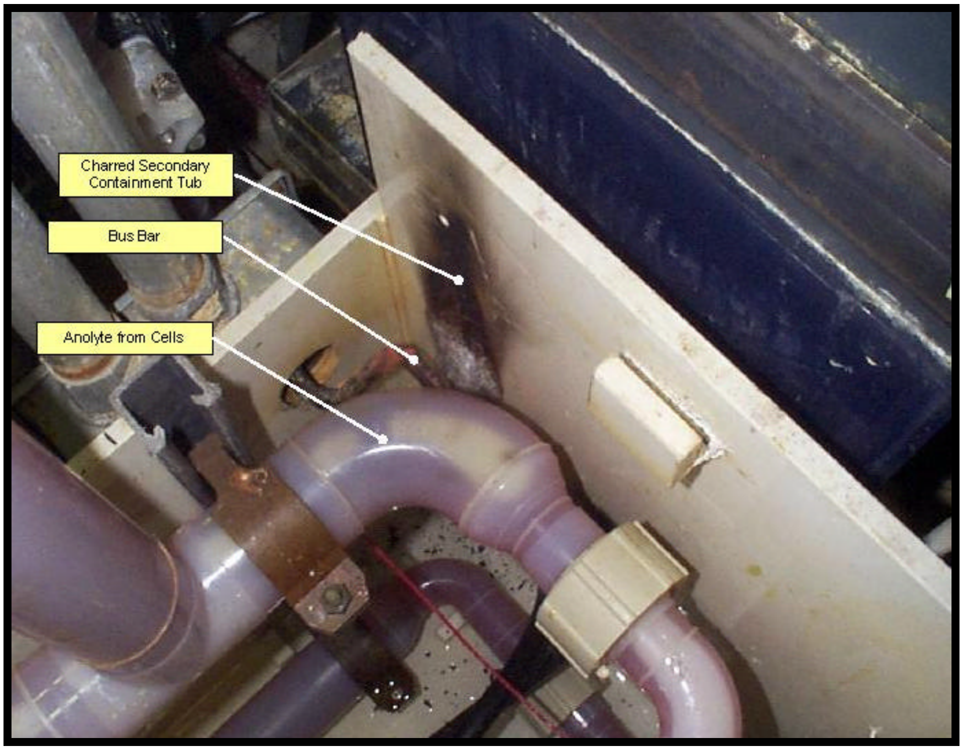
Figure 4-10 Process Temperature Monitoring Data - GB-2



4.2.8 Test Run GB-3

At 0800h June 5, 2001, during the normal warm-up sequence, a small fire was discovered in the processing unit. The source of the fire was an overheated bus bar adjacent to the secondary containment tub for the electrolytic cells. The overheated bus bar caused part of the secondary containment tub to burn with a small flame. Figure 4-11 shows the bus bar and associated damage to the secondary containment tub which was minimal. On discovery of the fire, CerOx aborted the warm-up sequence by pushing the abort enunciator on the control panel. CerOx extinguished the flame with water. A corroded fitting where two sections of the bus bar were assembled caused the excessive electrical resistance in the bus bar.

Figure 4-11 Bus Bar and Charred Secondary Containment



The initial configuration of the CerOx unit was a System 4, which contained 4 electrochemical cells. Bus bars were fabricated to fit this design. Since the bus bars are made of copper, which will corrode, a coating of black insulator material was applied. During the transformation to the two-cell design, the bus bars were reconfigured to fit the newly designed cells. When the pieces of the bars were bolted together, one of the bars had the black insulating coating between it and the connecting bar. This caused insulating material to be placed between the two bars, which created a situation where most of the current traveled through the bolt attaching the two bars. The bolt eventually corroded which caused increased electrical resistance through the bus bar. The bus bar was removed and the corrosion along with the remaining insulating material was removed using a grinder. The assembly was put back together with conducting grease and no further heating of the bus bar was observed.

At 0915h, the unit was restarted and immediately followed by a high level alarm in the NOx Absorbers. The unit was shut down and the level was reduced by manually turning on the column recirculation pump. The unit was restarted and the automatic warm-up sequence was continued.

Test Run GB-3 was an 8-hour validation run on June 5, 2001. Figure 4-12 shows the raw CEM data while Figure 4-13 shows some of the temperature profiles of process fluids from the CerOx SCADA system. The SOR was at 09:30h and had an initial flow rate set at approximately 2.4 kg/hr of the GB neutralent simulant. CerOx set the initial cell current at 450 amps. The make-up water flow rate to the Axi-Shear scrubber system was set at approximately 0.6 gpm.

TRC logged and recorded data measured in the stack gases from the unit using their CEM equipment. A summary of the stack data is shown in Figure 4-12. TRC also pulled the initial, intermediate, and final process samples for laboratory analyses.

At 1730h the 8-hr validation test was complete with a total of 19.2 kg of feed treated during the test, which resulted in an average feed rate of 2.4 kg/hr. During the test the anolyte was periodically measured for Ce^{+4} concentration and ranged from 0.57 to 0.69M. No unscheduled shutdowns occurred during the run.

Following the run, the normal shutdown sequence was followed.

Anolyte filter solids were extremely fine and were a greenish brown color. The quantity of solids was undetermined do to the complications associated with supplying filter samples to multiple laboratories for analysis and the fact that so little solids were generated. CerOx estimated the total solids generated at less than a couple of grams.

Figure 4-12 CEM Stack Gas Data (Raw) GB-3

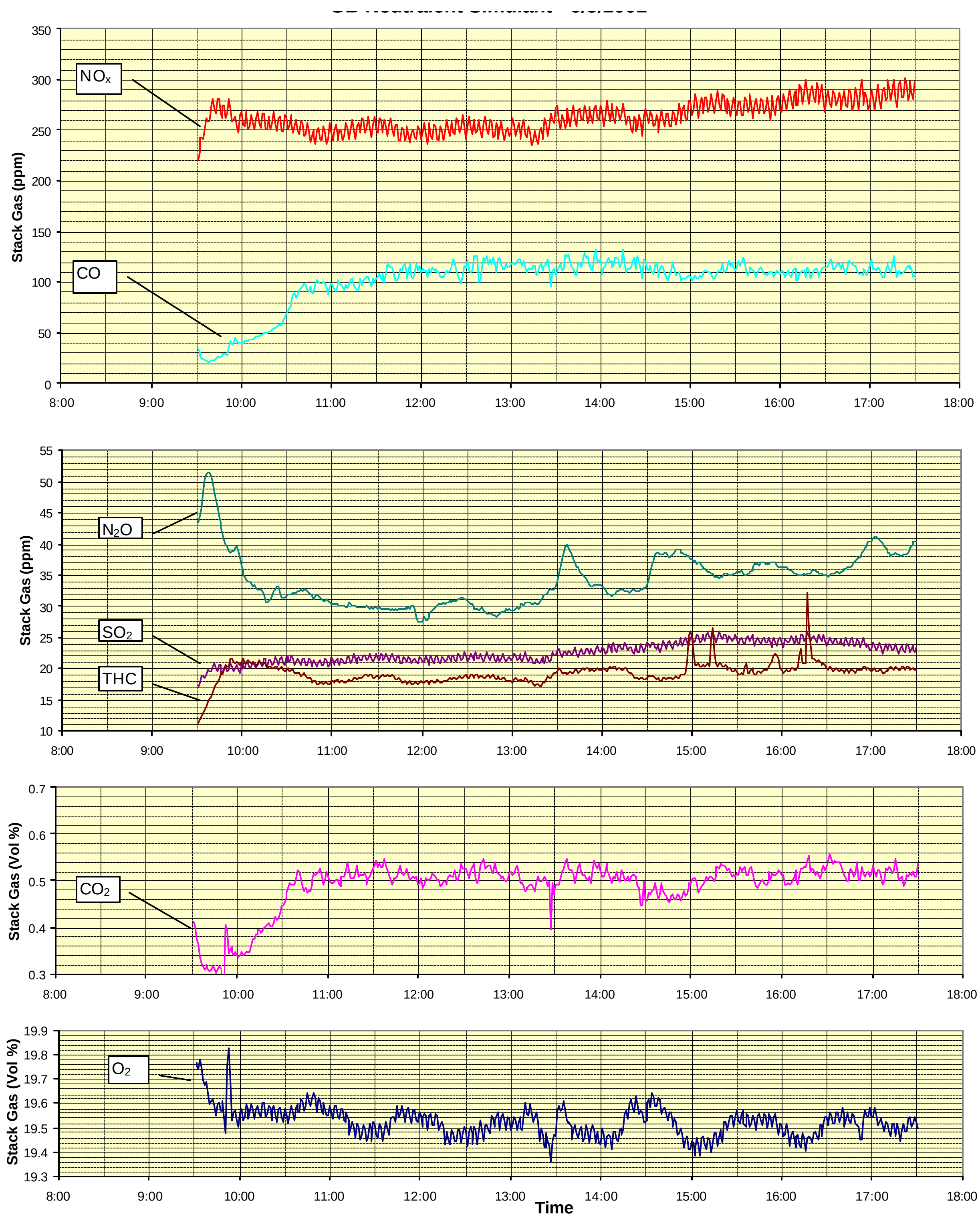
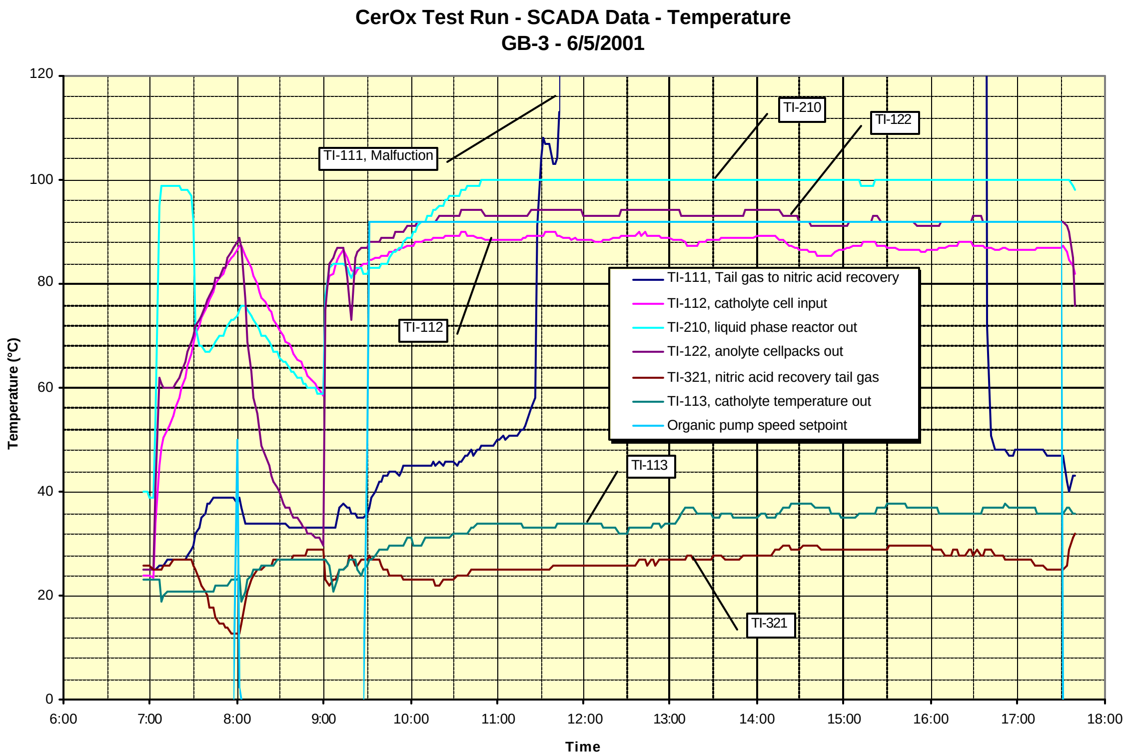


Figure 4-13 Process Temperature Monitoring Data - GB-3



4.3 Sampling and Analysis Description

The Sampling and Analysis activities were under the supervision of TRC. Their subcontract entailed oversight of the sample collection, transport of the samples to the respective laboratories, Quality Control/Quality Assurance associated with these tasks and reporting of the results. Southwest Research Institute (SwRI) was subcontracted to Stone & Webster and tasked with the analyses for schedule 2 and breakdown products. Philip Analytical (Ontario, Canada) was subcontracted by TRC to carry out all remaining analyses.

The CerOx/UNR personnel at the test facility were responsible for sampling and sample submission of feed materials, waste materials, process streams, and anolyte filter solids. TRC personnel were responsible for sampling stack gases and operating the CEM equipment. CerOx/UNR personnel were responsible for the collection of certain monitoring information, coordination and timing of sampling activities, and collection of system operating data.

The Sampling and Analysis Plan prepared by CerOx for this test program specified the collection of samples identified in Table 4-4. The location of specific sample locations can be seen in Figure 3-7 and Figure 3-8.

Table 4-4 Sample ID and Descriptions

Sample ID	Sample Description
SP-1	Liquid samples from HD and GB neutralent simulant feeds.
SP-2	Gas samples of the Stack gas from the CerOx Unit.
SP-3	Not used.
SP-4	Not used.
SP-5	Liquid samples from the scrubber effluent were collected from the Axi-Shear scrubber sump. These samples represent the scrubber effluent, which were collected in a 4000-gallon wastewater storage tank prior to release.
SP-6	Liquid samples from Caustic Solution Make-up to the CerOx Unit.
SP-7	Liquid samples of the Make-up water to the CerOx Unit.
SP-8	Gas samples of the compressed air to the NOx Absorber system.
SP-9	Liquid samples of the Nitric Acid Solution Make-up to the CerOx Unit.
SP-10	Liquid samples of the anolyte from the electrochemical cells to the Anolyte Tank.
SP-12	Liquid samples of the catholyte solution from the electrochemical cells to the Catholyte Tank.
SP-13	Gas samples of the ambient air that is drawn into the Axi-Shear system.
SP-14	Solid samples from the anolyte filters.
SP-15	Solid samples from the Axi-Shear system sump. No samples were taken since there were no solids observed.
SP-16	Liquid samples of the NOx Caustic Scrubber solution.

4.3.1 Sampling Locations

Thirteen sampling locations were identified for collecting representative samples of the feed, process, and effluents.

4.3.1.1 SP-1 – Feed Stream

The feed stream samples (SP-1) were usually taken at the beginning and end of a test campaign. Liquid samples were taken from the recirculation line from the Waste Organic Metering Pump (P-201). The neutralent simulant streams were analyzed for its initial components to detect any possible reaction. In addition, the samples were analyzed in a similar manner to other liquid effluents from the system to identify any contaminants or anomalies being fed to the system. The following parameters were scheduled for analysis:

- Cl, SO_4 (HD-2,3,4 only) and F, PO_4 (GB-2,3,4 only)
- TSS (Total Suspended Solids)

- VOCs (Volatile Organic Compounds)
- SVOCs (Semi-Volatile Organic Compounds)
- Al, Ce, Cr, Cu, Fe, Hg, Zn
- Total Organic Carbon (TOC), Total Inorganic Carbon (TIC)
- MEA (Monoethanolamine)
- DMSO (Dimethylsulfoxide) (HD-2,3,4 only)
- DMMP (Dimethyl methyl phosphonate), MPA (Methylphosphonic acid), DIMP (Diisopropyl methyl phosphonate), and EMPA (Ethylmethyl phosphonic acid) (GB-2,3,4 only)

4.3.1.2 SP-2 – Stack Gas

All gas sampling were conducted at the Axi-Shear exhaust duct. The parameters measured at the exhaust gas stack during the validation runs include:

- Flow rate
- Moisture
- MEA
- VOCs
- SVOCs
- CEM (Continuous Emission Monitoring) parameters (O_2, CO_2, NO_x, CO, THC, and N_2O)
- HCl, DMSO and Cl_2 (HD-2,3,4 only)
- HF, DMMP, MPA, DIMP, and EMPA (GB-2,3,4 only)

The Axi-Shear exhaust duct has a sample tap for the CEM line, a sample tap for TRC's sample manifold, a tap for temperature measurement, and a sample tap for measuring stack gas flow rates.

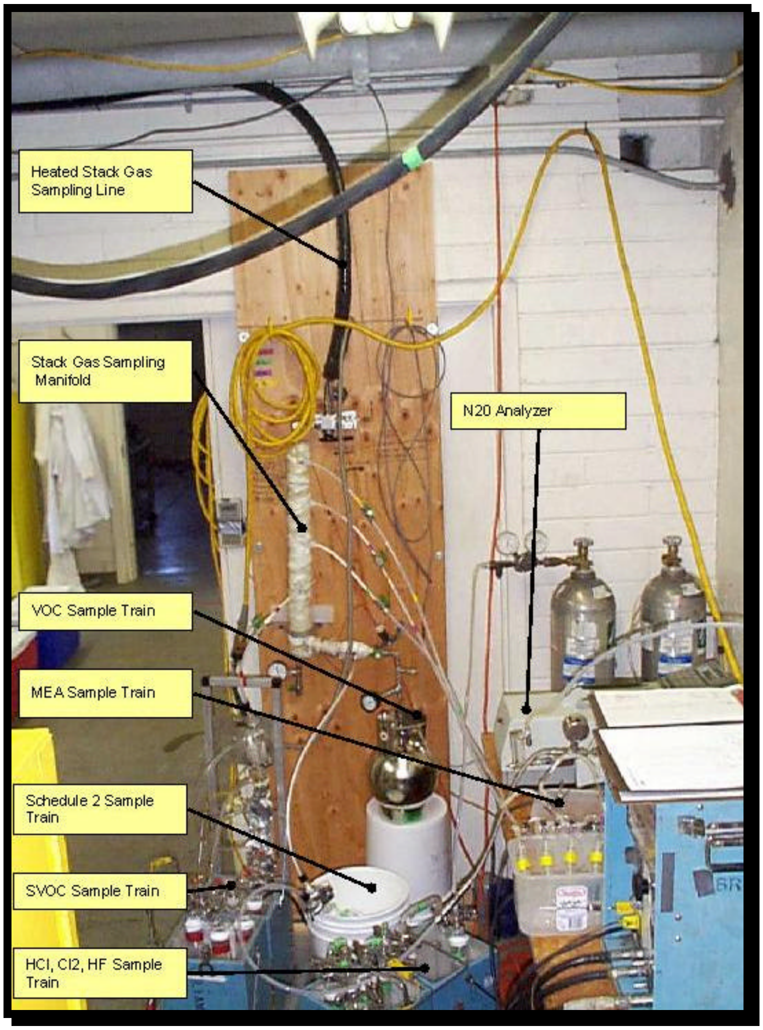
The CEM sampling train consisted a stainless-steel sampling probe, followed by a glass fiber filter, a heated (248°F ± 25°F) Teflon sample line, a sample conditioner, a double diaphragm pump which discharged to a stainless-steel sample manifold. The O_2, CO_2, NOx, CO and SO_2 analyzers withdrew samples from this manifold. The N_2O analyzer pulled its sample from the same heated sample line and manifold as the gaseous streams. A vacuum pump drew exhaust gases from the manifold through a knockout impinger and into the N_2O analyzer. The THC sample line was pulled off the heated line upstream of the sample conditioner (moisture removal was not required) and delivered to the THC analyzer.

Figure 4-14 CEM Analyzers and Recorders

TRC's sampling manifold was utilized to divert stack gas samples to 5 sampling trains. Sampling trains were set-up for the following parameters:

1. VOCs (Sampling method TO-15)
2. SVOCs (Sampling method M0010, modified)
3. HCl, Cl_2, HF (Sampling method M0050, Modified)
4. MEA (Sampling method NIOSH M2007)
5. DMSO, DMMP, MPA, DIMP, and EMPA (Sampling Method ACT-013)

Figure 4-15 Stack Gas Sampling Manifolds



4.3.1.3 SP-5 – Scrubber effluent

Scrubber effluent samples were taken from the sump of the Axi-Shear unit prior to discharge to the wastewater collection tank. Grab samples were normally collected at the beginning of a test run and at 4-hr intervals thereafter. The scrubber effluent samples were analyzed for feed components, along with several other analyses important to provide data to determine whether the test objectives have been met. The following parameters were scheduled for analyses:

- Cl, SO_4 (HD-2,3,4 only) and F, PO_4 (GB-2,3,4 only)
- TSS (Total Suspended Solids)
- VOCs
- SVOCs
- Al, Ce, Cr, Cu, Fe, Hg, Zn
- Total Organic Carbon (TOC), Total Inorganic Carbon (TIC)

- MEA
- DMSO (HD-2,3,4 only)
- DMMP, DIMP, MPA, EMPA (GB-2,3,4 only)

4.3.1.4 *SP-6 – Caustic Make-up*

Samples of the caustic solution injected into the Axi-Shear (caustic scrubber) unit were drawn from the caustic supply drum. Grab samples were scheduled to be collected once per test campaign (two in total). The following parameters were scheduled for analyses:

- Cl, SO_4 (HD-2,3,4 only) and F, PO_4 (GB-2,3,4 only)
- TSS (Total Suspended Solids)
- VOCs
- SVOCs
- Al, Ce, Cr, Cu, Fe, Hg, Zn
- Total Organic Carbon (TOC), Total Inorganic Carbon (TIC)

4.3.1.5 *SP-7 – Make-up Water*

Samples of the make-up water were taken from a sample port on the line feeding the Axi-Shear (caustic scrubber) unit. Samples were scheduled to be collected once per test campaign (two total). The make-up water samples were scheduled for the following analyses:

- Cl, SO_4 (HD-2,3,4 only) and F, PO_4 (GB-2,3,4 only)
- TSS (Total Suspended Solids)
- VOCs
- SVOCs
- Al, Ce, Cr, Cu, Fe, Hg, Zn
- Total Organic Carbon (TOC), Total Inorganic Carbon (TIC)

4.3.1.6 *SP-8 – Air to NOx Absorbers*

Samples of air, which is fed to the NOx Absorber system, was taken from a sample port on the compressed air line feeding the unit. The compressed air originates from the compressor system in the Advanced Research Facility Building. A compressed air supply line travels underground to the Annex Building were the CerOx System 2 is installed. Samples were scheduled to be collected once per test campaign (two total). The make-up air samples were scheduled for the following analyses:

- VOCs
- SO_2, NOx, O_2, CO_2, CO, N_2, H_2

4.3.1.7 *SP-9 – Nitric Acid Make-up*

Samples of nitric acid (36 to 42° Baumé), which is fed to the Catholyte Tank to maintain acid strength in the catholyte solution, were taken from the Nitric Acid drum. Samples were scheduled to be collected once per test campaign (two total). The make-up water samples were scheduled for the following analyses:

- Cl, SO_4 (HD-2,3,4 only) and F, PO_4 (GB-2,3,4 only)
- TSS (Total Suspended Solids)
- VOCs
- SVOCs
- Al, Ce, Cr, Cu, Fe, Hg, Zn
- Total Organic Carbon (TOC), Total Inorganic Carbon (TIC)

4.3.1.8 SP-10 – Anolyte

Samples of the anolyte solution (approximately 3M nitric acid and 1.5M total cerium) were taken from a sample port on the line returning the anolyte solution from the cells to the Anolyte Tank (TK-120). Samples were scheduled to be collected at the beginning and end of each run. Note that SOR samples were not taken if the EOR of the previous run were representative. The anolyte samples were scheduled for the following analyses:

- Cl, SO_4 (HD-2,3,4 only) and F, PO_4 (GB-2,3,4 only)
- TSS (Total Suspended Solids)
- VOCs
- SVOCs
- Al, Ce, Cr, Cu, Fe, Hg, Zn
- Total Organic Carbon (TOC), Total Inorganic Carbon (TIC)
- MEA
- DMSO (HD-2,3,4 only)
- DMMP, DIMP, MPA, EMPA (GB-2,3,4 only)

4.3.1.9 SP-12 – Catholyte

Samples of the catholyte solution (approximately 3M nitric acid) were taken from a sample port on the line returning the catholyte solution from the cells to the Catholyte Tank (TK-110). Samples were scheduled to be collected at the beginning and end of each run. Note that SOR samples were not taken if the EOR of the previous run were representative. The catholyte samples were scheduled for the following analyses:

- Cl, SO_4 (HD-2,3,4 only) and F, PO_4 (GB-2,3,4 only)
- TSS (Total Suspended Solids)
- VOCs
- SVOCs
- Al, Ce, Cr, Cu, Fe, Hg, Zn
- Total Organic Carbon (TOC), Total Inorganic Carbon (TIC)
- MEA
- DMSO (HD-2,3,4 only)
- DMMP, DIMP, MPA, EMPA (GB-2,3,4 only)

4.3.1.10 SP-13 – Make-up Air to Axi-Shear Unit

Samples of air, which is drawn into the Axi-Shear (caustic scrubber) Unit, were taken from a sample port located on the make-up air duct to the unit. Atmospheric air is drawn into the make-up air duct from an inlet on the West Side of the Annex Building. Samples were scheduled to be collected once per test campaign (two total). The make-up air samples were scheduled for the following analyses:

- VOCs
- SO_2, NOx, O_2, CO_2, CO, N_2, H_2

4.3.1.11 SP-14 – Anolyte Filter Solids

Samples of anolyte filter solids were taken from the anolyte filter and fluid remaining in the filter housing. The CerOx system was operated with filtration system (cartridge type) which removed solids (> 1 micron) from the anolyte solution. A slipstream from the Anolyte Supply Pumps (P-110) was passed through the filter and returned to the Anolyte Tank (TK-120). Upon completion of each test run, the filter housing was drained into a clean 5-gallon bucket. The filter was then removed and put into the same bucket. Since the samples had to be sent to separate labs, the filter had to be cut in half lengthwise. One-half of the filter and one-half of the mixed filter housing liquids were sent to each lab. The filter solids were scheduled for the following analyses:

- Cl, SO_4 (HD-2,3,4 only) and F, PO_4 (GB-2,3,4 only)
- Full TCLP
- VOCs
- SVOCs
- Al, Ce, Cr, Cu, Fe, Hg, Zn
- MEA
- DMSO (HD-2,3,4 only)
- DMMP, DIMP, MPA, EMPA (GB-2,3,4 only)

4.3.1.12 SP-15 – Caustic Scrubber Solids

Samples of caustic scrubber solids, which could accumulate in the Axi-Shear (caustic scrubber), were to be sampled. The lack of any observable solids prevented any samples from being collected during the tests. The solids were scheduled for the following analyses:

- Cl, SO_4 (HD-2,3,4 only) and F, PO_4 (GB-2,3,4 only)
- Full TCLP
- VOCs
- SVOCs
- Al, Ce, Cr, Cu, Fe, Hg, Zn
- MEA
- DMSO (HD-2,3,4 only)

- DMMP, DIMP, MPA, EMPA (GB-2,3,4 only)

4.3.1.13 SP-16 – NOx Caustic Scrubber Solution

The NOx Caustic Scrubber Solution samples were taken from the NOx Caustic Scrubber Drum. This sample location was not on the original Sampling and Analysis Matrix. Field inspection of the CerOx System 2 included the discovery of the NOx Caustic Scrubbing system, which had not been previously disclosed. SP-16 was subsequently added to the Sampling and Analysis matrix. Grab samples were normally collected at the SOR and at EOR. The following parameters were scheduled for analyses:

- Cl, SO_4 (HD-2,3,4 only) and F, PO_4 (GB-2,3,4 only)
- TSS (Total Suspended Solids)
- VOCs
- SVOCs
- Al, Ce, Cr, Cu, Fe, Hg, Zn
- Total Organic Carbon (TOC), Total Inorganic Carbon (TIC)
- MEA
- DMSO (HD-2,3,4 only)
- DMMP, DIMP, MPA, EMPA (GB-2,3,4 only)

5. OPERABILITY

This section presents Stone & Webster's comments on the design and operation of the CerOx System 2 Unit as observed during the Limited Engineering Scale Testing. Comments on the operation of the major equipment items and as well as observations on operational modes (with recommendations for modification), standard operating procedures, process safety and worker safety are provided.

The operations of the following subsystems were observed and are evaluated.

5.1 Electrochemical Cells

The initial system installed at UNR's facility was a CerOx System 4. This system is characterized by its 4 electrochemical cell packs. The system was later converted to a 2 electrochemical cell pack design, which would normally carry the CerOx System 2 designation. Several other modifications were made to the system based on testing requirements, improved efficiencies, and improved design elements. In preparation for this LEST, CerOx installed 2 new electrochemical cell packs which reflected their latest engineering design. These new cell packs were the same design as the CerOx System 4 being built for the University of California at Irvine (UCI). It was important to CerOx to test cells, which reflect their most current designs.

During the LEST, it was immediately apparent to CerOx that the new cells were more efficient in their ability to produce Ce^{+4}. To measure this efficiency, CerOx calculates the coulombic efficiency for the oxidation of Ce^{+3} to Ce^{+4}. In the previous generation cell design, CerOx measured coulombic efficiencies in the range of 77-80%. Based on data accumulated from this LEST, CerOx calculates a coulombic efficiency of 88.8%. This represents a nearly 10% efficiency improvement and is very close to the best efficiency (92%) obtained in the laboratory. CerOx claims that the engineering changes made to the injection molds for the cell parts are the source of increased efficiency.[8]

With the increased efficiency of the electrochemical cells to produce Ce^{+4}, came benefits with consequences. At a given cell current, the increased efficiency allowed for an increase in the formation of Ce^{+4}, which allowed an incremental increase in the organic feed rate while maintaining the desired Ce^{+4} concentration in the reactor. In this case, greater organic feed translated into greater organic destruction and greater heat generation from the heat of reaction.

The main heat sink for the anolyte solution is the electrochemical cell itself. The electrochemical cell acts similar to a plate-and-frame heat exchanger where the heat is transferred from the anolyte fluid to the catholyte fluid. As the heat is transferred to the catholyte, the temperature in the Catholyte Tank (TK-110) begins to rise. Heat removal from the catholyte loop is accomplish via the Catholyte Heat Exchanger (HX-111) which cools a slip stream of catholyte to be sent to the NOx Absorbers. A cool stream of recovered catholyte then returns to the Catholyte Tank (TK-110) from the NOx Absorber system. This effectively makes the Catholyte Heat Exchanger (HX-110) the main route of heat removal from the entire CerOx System.

The additional heat generated from the more efficient new cell design was evident in the HD-2 and HD-4 validation tests. In validation test HD-2, the temperature of the anolyte from the cells and the catholyte to the cells rose to 94°C and 97°C respectively.

At this point CerOx responded to the increased temperatures by reducing the current to the cells from 500 amps to 450 amps and effectively prevented any adverse fluid conditions (lower Joule Heating – electrical heating from the cell).

During the HD-4 run, the identical trend in temperatures occurred with the current to the cells set at 450 amps. This run had an added complication in that it was operating at a slightly increased organic feed rate. The temperatures in the catholyte loop rose to the point were cavitation was detected in the Catholyte Supply Pump (P-110). Pump cavitation (vaporization of fluid) occurs if the pressure at any point within the pump falls below the vapor pressure of the liquid being pumped. Since the catholyte solution was near its boiling point (vapor pressure of liquid equals system pressure), any pressure drop through the suction piping or within the pump itself will cause the fluid to vaporize. In conclusion, there was not enough heat removal capacity in the catholyte loop to prevent cavitation of the catholyte pump.

In order to combat the heat removal problem, CerOx reconfigured the heat exchanger arrangement in order to provide a trim cooler on the catholyte circulation loop (see the new position of HX-210 in Figure 3-8). This was accomplished by re-piping the Reactor Offgas Condenser (HX-210), which was not utilized in the previous tests because it has little impact on the process, to cool a slipstream of catholyte solution downstream of the Catholyte Supply Pump (P-110). A control valve, reset by the catholyte tank (TK-110) temperature, was installed on the cooling water supply line. This modification enabled the unit to have additional heat exchanger area available to help cool the catholyte solution. The effect of the new exchanger configuration can be seen in test run HD-3 where the TI-112 and TI-122 are 8 and 6°C cooler respectively than the previous test run HD-4. During subsequent runs, this modification gave the System 2 very good control of the catholyte circulation temperatures.

Test Run ID	TI-112 Anolyte from cells	TI-122 Catholyte to cells	TI-210 Anolyte from Liquid Phase Reactor	Time
HD-2	94	97	100	16:40h
HD-4	96	98	101	13:35h
HD-3	88	92	100	Typical

5.2 Reactor System Off-gas

There is competition between 2 anodic reactions in the CerOx technology. The first is the (desired) oxidation of Ce(III) to Ce(IV) and the second is the (parasitic) oxidation of water to oxygen. The Pt catalytic coating on the anode selects for the thermodynamically unfavorable Ce(III) oxidation reaction (E^o ~1.6v) over the energetically more favorable water oxidation (E^o ~ 1.4v). In both reactions, the cathode process is the reduction of nitric acid to nitrous acid. The oxidation of water does not generate hydrogen at the cathode unless the nitric acid concentration drops below the process set point. To prevent hydrogen formation the catholyte acid level is monitored by measurement of the solution conductivity. As the conductivity drops owing to nitric acid consumption, additional acid is added to maintain the conductivity set-point. If the conductivity set-point cannot be maintained the system shuts down.[9]

As mentioned above, the cerium oxidation reaction is in competition with the parasitic oxidation of water. The oxidation of water produces oxygen and hydrogen ions at the anode and the reduction of nitric acid at the cathode as shown in the following reactions:

$$Anode: \quad H_2O \rightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e^-$$

$$Cathode: 2H^+ + HNO_3 + 2e^- \rightarrow H_2O + HNO_2$$

It is important to note that molecular hydrogen is not involved in this process. The only time that molecular hydrogen can be generated is at the anode when the nitric acid level falls below the set point.[10] Given the scenario where the control system (conductivity probe) malfunctions and the concentration of nitric acid in the catholyte falls below the set point, a potential hazard (flammable conditions) could develop with the build up of hydrogen in the catholyte off-gas. Additional instrumentation to monitor hydrogen in the cathode off gas should be considered.

In addition, the generation of oxygen on the anode could create an oxygen rich environment where the presence hydrocarbons as a result of incomplete oxidization, could form a combustible atmosphere. Additional instrumentation to monitor oxygen in the anode off gas should be considered.

5.3 Gas Phase Reactor Design

The volatile nature of 1,2-dichloroethane (normal boiling point at ˜ 77°C[11] at Reno's elevation) and the fact that the Liquid Phase Reactor operated at approximately 100°C, probably allowed a significant portion of the 1,2-dichloroethane in the organic feed to pass through the Liquid Phase Reactor as part of its off-gas. Under this scenario, the 1,2-dichloroethane would pass to the Gas Phase Reactor. The Gas Phase Reactor is a packed column, which provides counter current contact of the Liquid Phase Reactor off-gas with fresh anolyte solution. The concept for this piece of equipment is to provide enough contact time to absorb the 1,2-dichloroethane into the anolyte solution where Ce^{+4} can oxidize it. This mass transfer limited reaction led to the conclusion by CerOx that there was inadequate contact time in the Gas Phase Reactor.

Note that 1,2-dichloroethane is only a component of the HD neutralent simulant. The simulant is designed to provide the proper ratios of carbon, sulfur, and chlorine as seen in the analysis of the actual NSCMP HD neutralent[12]. 1,2-dichloroethane was added to the simulant to provide the chlorine content identified in the actual HD neutralent. 1,2-dichloroethane is not detected in the analysis of the actual NSCMP HD neutralent[13]. Although 1,2-dichloroethane was not detected in the actual HD neutralent, this discussion could be applied to other VOCs, which are fed or generated in the Liquid Phase Reactor.

The Gas Phase Reactor should provide increased mass transfer in order to prevent VOC from exiting in the tail gas.

As part of their next generation design, CerOx has replaced the existing Gas Phase Reactor with a new design that provides 5 times the contact time as the previous reactor[14].

5.4 Ce^{+4} Control System

The System 2 at UNR had the capability of automatically adjusting the feed rate of organic waste material based on the concentration of Ce^{+4} entering and leaving the Liquid Phase Reactor (TK-210). Unfortunately, the sample valves to the in-process sensors were made of improper materials, which prevented their operation. CerOx manually sampled the anolyte solution and titrated to determine cerium concentration. Sample valves with proper materials of construction should be specified.

CerOx has reported that a new hydraulic system for the in-process analysis for Ce^{+4} has been designed[15].

5.5 Control System Sensitivity

CerOx has developed a control system, which is geared towards minimal operator interface. This is important for their current market customers, but can be made slightly more accommodating for more industrial users by alarming prior to shutdown for non-critical systems. In other words, if a non-critical system alarms, enunciate the alarm to the operator for confirmation. If no action is taken in a reasonable amount of time, then a full shutdown sequence can commence.

CerOx has reported that the above-mentioned suggestions to the control system have been implemented in the system for UC Irvine[16].

5.6 Solids in Liquid Phase Reactor

The HD and GB neutralent simulants contain some inorganic elements, which will not be treated by the CerOx process. CerOx reports that the inorganic elements accumulate in the anolyte solution as soluble salts until they reach a concentration where they begin to precipitate or diminish the effectiveness of the unit. The LEST did not attempt to run the unit to determine anolyte exhaustion. However, the presence of solids (inorganic precipitates) in the anolyte is a real concern.

The test plan estimated that approximately 8.3 lbs. of cerium fluoride and 30.7 lbs. of cerium phosphate would precipitate in the total combined GB neutralent simulant work-up and validation runs. The combined HD neutralent simulant runs were expected to generate 7.5 lbs. of cerium sulfate.[17] A small amount of solids (estimated at less than 2 grams per test) were formed in each test run and collected in the anolyte filter. The solids were very fine and required a considerable amount of time to settle out of the residual anolyte solution collected when the filter was removed. The minute amount of collected solids was clearly not expected. This would suggest that the solids did not form and the salts remained soluble in the anolyte. It may be necessary to further investigate the solids formation and life expectancy of the anolyte solution.

From a process point of view, the solids can cause some problems if they collect in a piece of equipment or piping. Plugging or settling of solids in the Liquid Phase Reactor (TK-120) which is in an up-flow configuration, or the electrochemical cells, or anolyte process line are possible examples solid plugging problems. Problems with solids in the anolyte were not observed but may need to be addressed in future designs.

5.7 NOx Absorber / NOx Caustic Scrubber

The NOx Absorber system is designed to recover nitrogen oxide gases, which are produced by the cathode reaction of nitric acid. Following the NOx Absorber system is a NOx Caustic Scrubber system. This system is designed to remove NOx gases by contact with a 25% caustic solution. In general, CerOx believes that the NOx Absorber system is undersized and more nitric acid recovery could be accomplished by increasing the effective height of the NOx Absorber Columns. The NOx Caustic Scrubber is really just a make shift piece of equipment that was added the CerOx Unit (outside unit) to help remove excess NOx from the tail gas of the NOx Absorber system. The optimization of this design is suspect since the column is a retrofit of an existing experimental process unit that had been abandoned. The unit is additionally hampered because the circulating caustic solution did not have a caustic make-up system. The CEM equipment measured a steady increase in the NOx concentration in the stack gases from the unit. When the NOx readings in the stack gases became relatively high (CEM data), CerOx removed some of the spent caustic solution from the NOx Caustic Scrubber Drum and charged the drum with fresh 25% caustic solution. This had an immediate impact on the NOx concentration in the stack gases from the unit. It was not uncommon to see the NOx concentration in the stack gases to drop 50% with the addition of fresh caustic solution.

The next generation CerOx System being built for UCI, has nearly 2 times the effective height for the NOx absorption system and does not have a dedicated NOx caustic scrubber. Instead, the anticipated improved efficiency of the NOx absorber systems allows the tail gases to be combined with the reactor off gas stream which is scrubbed in a newly designed Alkali Scrubber system (replacing the Axi-Shear Scrubber).

5.8 Axi-Shear

The Axi-Shear unit is used to remove acid gases from the combined reactor off gas stream and the residual NOx tail gas stream. Inherent to the design, is a make-up air stream that is drawn into the system upstream of the unit. The make-up air is necessary to satisfy the needs of the blower, which pulls the gases through the unit. Traditional scrubbing systems do not require make-up air to be drawn into the unit.

CerOx's design of the UCI system shows a more traditional scrubber that does not require make-up air. This new system should provide performance, which closely matches that of traditional scrubbing systems. A standard scrubber is planned to replace the Axi-Shear system in the UNR System 2.

5.9 Nitric Acid Pump

The Nitric Acid Addition Pump (P-401) is used to add nitric acid to the Catholyte Tank (TK-110) to maintain acid strength and to compensate for acid losses from un-recovered NOx gases and other vent losses. The positive displacement pump with stroke and speed controls periodically lost efficiency by trapping vapor in the suction line. This caused the pump to push very little nitric acid into the system.

On June 5, 2001 CerOx installed a new nitric acid pump system, which uses the same valve-less pumping technology as the organic feed pump. The pumping system was installed with a three way valve to recycle the nitric acid when no forward flow is required and a flow switch to detect no flow in a situation were the control system demands flow. This system is an improvement to the previous design and showed that it could prime a line full of vapor.

6. TEST RESULTS & DISCUSSION

6.1 Stream Characterization

The SAP specified analyses of each liquid feed stream to be used for the CerOx LEST. Scheduled analyses are discussed in Section 4.3.1.1.

6.1.1 HD Neutralent Simulant

The HD Neutralent Simulant is a blend of MEA, 1,2-dichloroethane, Dimethylsulfoxide and water in proportions outlined in Table 4-1. The simulant was prepared using the Simulant Preparation Procedure[18] prepared by SwRI. Note that CerOx/UNR prepared the mixture exactly according to the instructions from SwRI[19].

Table 6-1 shows the results of the analyses performed on grab samples from the neutralent feed drum along with the expected concentrations of key components based on the simulant preparation. Comparing the expected concentrations with the actual analyses shows a fair amount of discrepancies. The expected TOC concentration of the HD neutralent simulant was 357,000 mg/L but the analyses show an average concentration of 270,000 mg/L (H-2 sample disregarded due to obvious misrepresentation). The total chloride results are reasonable with an average of 24,300 vs. 26,400 mg/L expected. MEA, which should make up nearly 83 wt% of the solution based on the preparation procedure, shows up in the analyses with an average concentration of 52 wt% which is grossly less than expected. In addition, 1,2-dichlorethane averaged 500 mg/L, which is orders of magnitude less than the expected concentration of about 35,000 mg/L. The expected concentration of DMSO was 28,700 mg/L. DMSO was found to be undetected in one of the samples (H-4) and reported at a maximum concentration of 6900 mg/L in sample H-3.

The clear discrepancy between the expected component concentrations in the feed and the reported concentrations from the analytical laboratory indicates problems with the feed preparation procedure and/or laboratory analysis methods. The indication of acetone, bromomethane, chloroform, and vinyl chloride in the simulant mixtures are unexplained. Although the preparation procedure indicated that no by-products were produced when the solution was prepared at room temperature, CerOx believes that vinyl chloride was produced in the neutralent simulant mixture via a dehydrohalogenation reaction between 1,2-dichloroethane and MEA[20]. Although this may explain why 1,2-dichloroethane was detected at levels below expected, it does not explain the presence of acetone, bromomethane, and chloroform.

Further investigations on the simulant preparation procedures and possible reactions were conducted by performing additional tests at SwRI. HD neutralent simulant mixtures were produced at various temperatures (25, 32 and 43°C) and tested for reaction products via NMR spectroscopy. Results indicated no change in the NMR spectrum for the three cases. In addition, the NMR spectrum showed the unreacted initial components and no byproducts. These results would indicate a problem with the analytical laboratory methods used determine simulant concentrations.

Table 6-1 HD Neutralent Simulant Analyses

Run ID / Run Hour / Date of Sample	Units	H-2 / 0 / 05/23/01	H-3 / 0 / 05/30/01	H-3 / 8 / 05/30/01	H-4 / 0 / 05/24/01	EXPECTED
INORGANIC + MISCELLANEOUS						
Aluminum	mg/L	NA	0.35	<0.030	2	
Cerium	mg/L	NA	7.9	5.5	6.4	
Chromium	mg/L	NA	<0.04	<0.040	<0.040	
Copper	mg/L	NA	0.19	0.12	<0.060	
Iron	mg/L	NA	0.71	0.79	0.24	
Mercury	mg/L	NA	0.033	0.012	0.041	
Zinc	mg/L	NA	1.1	1.1	1.1	
pH	mg/L	NA	11.59	11.47	11.88	
TSS	mg/L	NA	850	1400	1200	
TIC	mg/L	34	30	37	<100	
TOC	mg/L	5.2	230,000	250,000	330,000	357,000
Chloride	mg/L	NA	21,000	25,000	27,000	26,400
Sulfate (as SO4)	mg/L	NA	<100	<100	<100	
VOC - LIQUID						
Acetone	µg/L	NA	140,000	130,000	140,000	
Bromomethane	µg/L	NA	1900	<5000	<5000	
2-Butanone	µg/L	NA	<3200	<16000	<16000	
Chloroform	µg/L	NA	2000	<2000	2700	
Chloromethane	µg/L	NA	<1400	<7000	<7000	
Dichlorobromomethane	µg/L	NA	<400	<2000	<2000	
1,2-Dichloroethane	µg/L	NA	5,700	1,400,000	27,000	36,800,000
Methylene Chloride	µg/L	NA	<2300	<12000	<12000	
Tetrachloroethene	µg/L	NA	1200	<2500	3500	
1,1,2-Trichloroethane	µg/L	NA	<600	<3000	<3000	
Trichloroethene	µg/L	NA	2000	<5000	<5000	
Vinyl Chloride	µg/L	NA	76,000	130,000	520,000	
SVOC - LIQUID			**(Note 1)**	**(Note 1)**		
		NA	NA	NA	NA	
MEA - LIQUID						
MEA - Ethanolamine	mg/L	NA	480,000	590,000	550,000	859,000
Schedule 2						
DMSO	?g/µL	NA	3800	6900	1000 U	31,400
Comments						

Notes:
(1) No analysis possible due to oiliness of sample.
(2) NA = No sample collected or no sample analyzed.
< = Not detected at detection limit.
U = Not detected at detection limit.

6.1.2 GB Neutralent Simulant

The GB Neutralent Simulant is a blend of MEA, DMMP, Ammonium Fluoride, and water in proportions outlined in Table 4-1. The simulant was prepared using the Simulant Preparation Procedure[21] prepared by SwRI. Note that CerOx/UNR prepared the mixture exactly according to the instructions from SwRI[22].

Table 6-2 shows the results of the analyses performed on grab samples along with the expected concentrations of key components. Comparing the expected concentrations with the reported concentrations from the analyses shows a fair amount of discrepancies. The expected TOC concentration of the GB neutralent simulant was 180,000 mg/L and analyses showed reasonable agreement with an average concentration of 160,000 mg/L. The total fluoride results are a bit more variable and averaged 13,900 vs. 9,000 mg/L expected. MEA, which makes up nearly 40 wt% of the solution, averages 29 wt% in the sample analyses. In addition, the concentration of DMMP reported in the GB neutralent simulant mixture ranged from 0.59 to 790 mg/L, which is grossly less than the expected concentration of 61,200 mg/L.

Acetone is reported in all of the GB neutralent simulant samples with concentrations ranging from 61,000 to 64,000 ug/L. The indication of acetone is unexplained since the GB neutralent simulation preparation procedure does not indicate the likelihood of chemical reactions. Nevertheless, it seems likely that the DMMP has either reacted or decomposed. Further investigation is required to explain these discrepancies.

Table 6-2 GB Neutralent Simulant Analyses

Run Number Run Hour Date of Sample	Units	G-3 8 06/05/01	G-4 0 06/01/01	EXPECTED
INORGANIC and MISCELLANEOUS				
Aluminum	mg/L	0.43	0.36	
Cerium	mg/L	0.024	<0.010	
Chromium	mg/L	0.7	0.68	
Copper	mg/L	0.09	<0.060	
Iron	mg/L	0.44	0.19	
Mercury	mg/L	0.017	0.0025	
Zinc	mg/L	0.64	0.6	
pH	mg/L	11	10.97	
TSS	mg/L	790	1500	
TIC	mg/L	44	24	
TOC	mg/L	160,000	160,000	180,000
Fluoride	mg/L	9,800	18,000	9,000
ortho-Phosphate (as P)	mg/L	<100	<100	
VOC - LIQUID				
Acetone	µg/L	64,000	61,000	
Bromomethane	µg/L	540	120	
Chloroform	µg/L	510	640	
1,2-Dichloroethane	µg/L	580	<40	
SVOC - LIQUID		**(Note 1)**	**(Note 1)**	
		NA	NA	
MEA - LIQUID				
MEA - Ethanolamine	mg/L	210,000	400,000	413,000
Schedule 2				
DMMP	µg/L	590	790,000	61,200,000
DIMP	µg/L	740	820	
EMPA*	mg/L	22,441	25,432	
Comments				

Notes:

(1) No analysis possible due to oiliness of sample.

(2) The EMPA results include IMPA & MMP, which coelute with EMPA.

(3) NA = Sample not collected or sample not analyzed

< = Not detected at detection.

6.1.3 Make-up Water

The analyses received for make-up water are summarized in Table 6-3. All detected VOCs and SVOCs were reported in the low µg/L range. Of particular interested is the detection of 90 µg/L of DMMP in the make-up water. This is probably attributable to laboratory error where residual material from a previous analysis is detected.

Table 6-3 Make-up Water Analyses

Run Number Run Hour Date of Sample	Units	G-2 0 06/04/01
INORGANIC AND MISCELLANEOUS		
Aluminum	mg/L	<0.03
Cerium	mg/L	0.014
Chromium	mg/L	<0.004
Copper	mg/L	0.2
Iron	mg/L	<0.010
Mercury	mg/L	<2.5
Zinc	mg/L	<0.01
pH	mg/L	NA
TSS	mg/L	5.7
TIC	mg/L	8.7
TOC (uv/persulf)	mg/L	0.73
Chloride	mg/L	NA
Fluoride (probe)	mg/L	<5.0
ortho-Phosphate (as P)	mg/L	NA
Sulfate (as SO4)	mg/L	<10
VOC - LIQUID		
Bromomethane	µg/L	1.7
Chloroform	µg/L	45
Chloromethane	µg/L	6.6
Dichlorobromomethane	µg/L	4.5
Methylene Chloride	µg/L	2.7
SVOC - LIQUID		
		ND
MEA - LIQUID		
MEA - Ethanolamine	mg/L	NA
Schedule 2		
DMSO	?g/µL	10 U
DMMP	µg/L	90
Comments		

Notes:
(1) ND = Not Detected at detection limit.
NA = Not collected or analyzed.
< = Not detected at detection limit.
U = Not detected at detection limit.

6.1.4 Make-up Air

A summary of the make-up air analyses is shown in Table 6-4. Make-up air to the NOx Absorbers is represented by sample location SP-08. Do to a field error, the valve to the SUMMA canister for sample collection was left in the closed position. This was determined when the laboratory measured the pressure in the SUMMA canister from the field and found that it had the practically the same pressure as the unsampled original. There were no other samples of the make-up air the NOx Absorber (compressed air system) taken during the LEST.

The make-up air to the Axi-Shear Scrubber is represented by sample location SP-13. This sample is representative of the background ambient air concentrations. 1,2-dichloroethane (0.141 mg/m^3) and ethanol (12.1 mg/m^3)

were detected. The likely source of contaminates comes from the fact that the CerOx unit is located in the UH&S Annex Building. This building is dedicated to UNR's waste management activities including handling, consolidation, temporary storing, and shipping of waste.

Table 6-4 Make-up Air Analyses

Sample Location		SP-08	SP-13
Sample Description		Make-up Air	Make-up Air
Run Number		H-3	H-3
Run Hour	Units	0	0
Date of Sample		05/24/01	05/24/01
MISCELLANEOUS			
SO_2		NA	NA
NO_x		NA	NA
O_2		NA	NA
CO_2		NA	NA
N_2		NA	NA
H_2		NA	NA
VOC - GAS			
Acetone	µg/m3	NA	<133
Benzene	µg/m3	NA	<240
Bromomethane	µg/m3	NA	<553
Chloroform	µg/m3	NA	<546
Chloromethane	µg/m3	NA	<101
1,2-Dichloroethane	µg/m3	NA	<391
Dichloromethane	µg/m3	NA	141
1,2-Dichloropropane	µg/m3	NA	<1034
cis-1,3-Dichloropropene	µg/m3	NA	<508
Ethanol	µg/m3	NA	12076
Hexane	µg/m3	NA	<466
1,1,2-Trichloroethane	µg/m3	NA	<721
Toluene	µg/m3	NA	<337
Vinyl Chloride	µg/m3	NA	<156
Comments		Note 2.	

Notes:

(1) NA = Sample not collected or analyzed.
< = Not detected at detection limit.

(2) SUMMA canister registered nearly identical vacuum as originally

6.1.5 Make-up Consumables

A summary of the analyses performed on grab samples of the 25% Caustic Solution and 36° to 42° Baumé Nitric Acid Solution make-up is illustrated in Table 6-5. The only reported VOC in the caustic was bromomethane at 0.061 mg/L. The inorganics included 7100 mg/L chlorides, which was probably due to the chlor-alkali process to manufacture caustic and chlorine from brine. TOC was reported at 12 mg/L.

Analyses of the nitric acid solutions reported the following hydrocarbons: bromomethane, chloroform, chloromethane, methylene chloride, and nitrobenzene. The nitric acid samples taken during the initial work-up run with HD neutralent simulant (HD-1) proved to have the heaviest concentration of hydrocarbons including 270 mg/L of chloroform and surprisingly, 1600 mg/L of sulfate was also detected. CerOx reported that one of the drums of 42° Baumé nitric acid had a noticeable organic-like liquid floating on the surface. This could account for the high chloroform levels reported.[23]

The nitric acid samples also reported a variety of metal concentrations, which are shown in Table 6-5. DMMP was detected in the nitric acid sample taken on 06/05/01 at 0.066 mg/L and was probably attributable to laboratory error.

Table 6-5 Caustic and Nitric Acid Analyses

Sample Location		SP-06	SP-09	SP-09
Sample Description		Caustic Make-up	Nitric Acid Make	Nitric Acid Make
Run Number		H-1	H-1	G-3
Date of Sample		05/23/01	05/23/01	06/05/01
INORGANIC AND MISCELLANEOUS				
Aluminum	mg/L	11	1.5	5.8
Cerium	mg/L	<0.05	1	<0.010
Chromium	mg/L	0.34	2.7	2.7
Copper	mg/L	0.11	1.5	0.069
Iron	mg/L	2.6	13	13
Mercury	mg/L	0.0038	0.13	<0.031
Zinc	mg/L	0.31	0.14	0.16
pH	mg/L		NA	1
TSS	mg/L	2000	53	13
TIC	mg/L	50	<10	<10
TOC (uv/persulf)	mg/L	12	17	5.1
Chloride	mg/L	7100	<50	NA
Fluoride (probe)	mg/L	NA	NA	<50
ortho-Phosphate (as P)	mg/L	NA	NA	<100
Sulfate (as SO4)	mg/L	<100	1600	NA
VOC - LIQUID				
Acetone	µg/L	<320	<25000	<1300
Acrolein	µg/L	<130	<10000	<510
Benzene	µg/L	<13	<1000	<50
Bromomethane	µg/L	61	2400	160
2-Butanone	µg/L	<80	<6400	<320
Chloroform	µg/L	<10	270,000	6200
Chloromethane	µg/L	<35	5700	<140
Dichlorobromomethane	µg/L	<10	<800	<40
1,2-Dichloroethane	µg/L	<10	<800	<40
Methylene Chloride	µg/L	<58	29,000	590
Vinyl Chloride	µg/L	<23	<1800	<90
SVOC - LIQUID				
2,6-Dinitrotoluene	µg/L	<1.2	<3.0	<30
Benzoic acid	µg/L	<10	<25	<250
Benzyl butyl phthalate	µg/L	<1.2	<3.0	<30
Bis(2-ethylhexyl)phthalate	µg/L	<2.8	<7.0	<70
Di-n-butyl phthalate	µg/L	<2.2	<5.5	<55
Nitrobenzene	µg/L	<4.0	290	<100
N-Nitrosodimethylamine	µg/L	<20	<50	<500
MEA - LIQUID				
MEA - Ethanolamine	mg/L	NA	NA	NA
Schedule 2				
DMSO	?g/µL	NA	NA	NA
DMMP	µg/L	NA	NA	66
Comments				

Notes:
(1) The EMPA results include IMPA & MMP, which coelute with EMPA.
(2) NA = Sample not taken or sample not analyzed.
U = Undetected at detection limit.
< = Undetected at detection limit.

6.1.6 Scrubber Effluent Analysis

The analyses for the HD neutralent simulant test runs are shown in Table 6-6. TOC ranged from 2 to 5.2 mg/L for the validation runs. The VOCs are all reported in the low µg/L range except for 1,2-dichloroethane in the H-2 and H-3 runs which ranged from 0.69 to 1.9 mg/L. All validation test reported less than 2 mg/L Total VOCs.

Benzyl butyl phthalate, Di-n-butyl phthalate, and nitrobenzene were detected in the very low µg/L ranges. CerOx believes that phthalates are plasticizer materials, which were most likely leached from the PVC (polyvinyl chloride) piping used for water service in the CerOx System 2[24].

In the scrubber effluent sample taken at the end of test run H-3, 86 µg/L DMMP was reported. This analysis was performed due to a sample Chain-of-Custody error. DMMP is a feed component of GB neutralent simulant, which had not been introduced into the System 2. The source of the 86 µg/L DMMP is probably due to laboratory error. DMSO was reported at less than 10 mg/L for all scrubber effluent samples analyzed.

The analyses for the GB neutralent simulant test runs are show in Table 6-7. TOC ranged from 1.6 to 56 mg/L for the validation runs. The TOC reported for runs G-3 seem excessively high when compared to the total VOCs and SVOCs detected and is most likely attributed to laboratory error. Further investigation is being conducted for possible laboratory errors.

1,2-dichloroethane, which is a feed material for the HD neutralent simulant test runs, was detected in the first GB neutralent simulant run (G-4 at 0 hours) at 0.06 mg/L. This is most likely attributable to the residual concentrations remaining in the CerOx System 2 after the HD neutralent simulant runs. During subsequent tests, the concentration of 1,2-dichloroethane steadily decreased until it was reported as undetected during the last chronological run (G-3).

As in the HD neutralent simulant runs, Benzyl butyl phthalate and Di-n-butyl phthalate were detected in the very low µg/L ranges.

DMMP was reported in GB neutralent simulant run numbers G-2 and G-3. The maximum level detected was in run number G-3 (8 hr mark) where the concentration was reported at 0.1 mg/L. MEA analyses for the scrubber effluent samples taken during the GB neutralent simulant test runs were normally reported at below detection limit which was 0.2 mg/L.

Table 6-6 Scrubber Effluent Analyses (HD Neutralent Simulant Runs)

Run Number	Units	H-1	H-2	H-2	H-3	H-3	H-4	H-4	H-4	H-4	H-4
Run Hour		0	0	8	4	8	0	4	8	16	24
Date of Sample		05/23/01	05/23/01	05/23/01	05/30/01	05/30/01	05/24/01	05/24/01	05/24/01	05/25/01	05/25/01
INORGANIC AND MISCELLANEOUS											
Aluminum	mg/L	0.06	0.038	0.038	0.043	0.093	0.047	0.052	0.089	0.031	0.088
Cerium	mg/L	0.15	0.054	0.055	0.072	0.081	0.25	0.044	0.048	0.071	0.036
Chromium	mg/L	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
Copper	mg/L	0.039	0.081	0.069	0.054	0.053	0.078	0.083	0.09	0.062	0.061
Iron	mg/L	0.035	0.038	0.025	0.02	0.014	0.044	0.023	0.035	0.012	0.039
Mercury	mg/L	<0.00005	<0.00005	<0.00005	<0.00005	<2.5	<0.00005	<0.00005	<0.00005	<0.00005	<0.00005
Zinc	mg/L	0.046	0.31	0.22	0.19	0.13	0.25	0.22	0.27	0.21	0.18
pH	mg/L	9.63	9.45	9.51	8.86	8.33	8.67	9.49	9.27	9.15	8.09
TSS	mg/L	<2.0	<2.0	2	<2.0	8	<2.0	<2.0	<2.0	<2.0	<2.0
TIC	mg/L	28	34	33	26	25	13	31	40	39	26
TOC	mg/L	25	5.2	4	3.3	4	2	3.6	4.4	4.3	4.3
Chloride	mg/L	9.4	15	16	11	NA	12	16	19	19	18
Fluoride (probe)	mg/L	NA	NA	NA	NA	<5.0	NA	NA	NA	NA	NA
ortho-Phosphate (as P)	mg/L	NA	NA	NA	NA	<10.0	NA	NA	NA	NA	NA
Sulfate (as SO4)	mg/L	3.8	4.3	4.3	3.8	NA	6.4	3.9	4.1	4.1	4.2
VOC - LIQUID											
Bromomethane	µg/L	NA	5.5	NA	30	7.3	18	16	18	18	27
2-Butanone	µg/L	NA	5	NA	<3.2	<3.2	5.2	7.9	5.4	4.4	<3.2
Chloroform	µg/L	NA	18	NA	4.8	9.4	34	13	30	31	22
Chloromethane	µg/L	NA	130	NA	26	10	5.5	22	12	7.5	30
1,2-Dichloroethane	µg/L	NA	690	NA	1900	1700	46	150	130	86	67
Methylene Chloride	µg/L	NA	16	NA	6.9	9.5	9.5	9.2	17	19	19
1,1,2-Trichloroethane	µg/L	NA	3	NA	1.5	1.5	0.6	1	1.1	2	2.1
Vinyl Chloride	µg/L	NA	<0.9	NA	<0.9	1.2	<0.9	<0.9	<0.9	0.9	<0.9
SVOC - LIQUID											
Benzyl butyl phthalate	µg/L	NA	2.7	2.2	5.8	5.1	2.6	1.9	3.9	<12	3.9
Di-n-butyl phthalate	µg/L	NA	<1.1	1.2	2.1	1.3	<1.1	2.2	1.2	<22	<1.1
Nitrobenzene	µg/L	NA	<2	<2	<2.0	<2.0	<2	<2.0	<2	<40	<2
MEA - LIQUID											
MEA - Ethanolamine	mg/L	NA	<0.2	<0.2	NA	NA	<0.2	<0.2	<0.2	<0.2	<0.2
Schedule 2											
DMSO	?g/µL	NA	10 U	10 U	10 U	10 U	10 U	10 U	10 U	10 U	10 U
DMMP	µg/L	NA	NA	NA	NA	86	NA	NA	NA	NA	NA
Comments											

Notes:
(1) NA = Sample not taken or sample not analyzed.
U = Undetected at detection limit.
< = Undetected at detection limit.

Table 6-7 Scrubber Effluent Analyses (GB Neutralent Simulant Runs)

Run Number		G-2	G-2	G-3	G-3	G-4	G-4	G-4	G-4	G-4
Run Hour	UNITs	0	8	4	8	0	4	8	16	24
Date of Sample		06/04/01	06/04/01	06/05/01	06/05/01	06/01/01	06/01/01	06/01/01	06/02/01	06/02/01
INORGANIC AND MISCELLANEOUS										
Aluminum	mg/L	0.065	0.54	0.077	0.059	0.11	0.067	0.072	0.084	0.094
Cerium	mg/L	0.054	0.16	0.2	0.09	2.2	0.089	0.09	0.41	0.12
Chromium	mg/L	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	0.006	<0.004
Copper	mg/L	0.031	0.032	0.034	0.035	0.043	0.039	0.037	0.035	0.034
Iron	mg/L	0.013	<0.01	<0.01	0.014	0.027	0.015	0.038	0.017	0.02
Mercury	mg/L	<0.0025	<2.5	<2.5	<2.5	<0.00005	<0.00005	<0.00005	<0.00005	<0.00005
Zinc	mg/L	0.073	0.054	0.053	0.055	0.18	0.077	0.067	0.064	0.07
pH	mg/L	11.96	NA	8.49	8.88	10.34	9.76	9.39	9.26	9.36
TSS	mg/L	2.3	5	<2	4.3	<2	<2	<2	<2	<2
TIC	mg/L	<18	13	22	23	5.6	13	11	15	14
TOC	mg/L	4.5	4.6	56	55	1.6	3.9	4.7	6.3	6.2
Chloride	mg/L	NA	NA	NA	NA	NA	NA	NA	NA	NA
Fluoride	mg/L	<50	<5	<5	NA	0.5	0.39	0.43	0.46	0.83
ortho-Phosphate (as P)	mg/L	<100	<10	<10	NA	<0.1	<0.1	<0.1	<0.1	<0.1
Sulfate (as SO4)	mg/L	NA	NA	NA	NA	NA	NA	NA	NA	NA
VOC - LIQUID										
Bromomethane	µg/L	96	25	33	17	4.8	NA	7.8	7.3	6.3
2-Butanone	µg/L	<3.2	<3.2	<3.2	<3.2	<3.2	NA	3.6	<3.2	<3.2
Chloroform	µg/L	3	3.8	4.3	3.3	10	NA	6.6	4.3	4
Chloromethane	µg/L	13	44	7.7	7	<1.4	NA	5.6	4	3.7
1,2-Dichloroethane	µg/L	0.4	0.5	<0.4	<0.4	60	NA	0.8	0.5	<0.4
Methylene Chloride	µg/L	<2.3	<2.3	<2.3	<2.3	<2.3	NA	<2.3	<2.3	<2.3
1,1,2-Trichloroethane	µg/L	<0.6	<0.6	<0.6	<0.6	<0.6	NA	<0.6	<0.6	<0.6
Vinyl Chloride	µg/L	<0.9	<0.9	<0.9	<0.9	<0.9	NA	<0.9	<0.9	<0.9
SVOC - LIQUID										
Benzyl butyl phthalate	µg/L	<5.3	6.6	8.9	9.2	0.7	4.5	6.3	7	6.6
Di-n-butyl phthalate	µg/L	<5.5	2	1.5	1.7	<1.1	1.5	1.7	1.6	<4.4
Nitrobenzene	µg/L	<10	<20	<20	<20	<2	<2	<2	<2	<8
MEA - LIQUID										
MEA - Ethanolamine	mg/L	<0.2	<0.002	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Schedule 2										
DMSO	?g/µL	1000 U	1000 U	NA	NA	NA	NA	NA	NA	NA
DMMP	µg/L	92	84	20 U	100	20 U	20 U	20 U	20 U	NA
Comments										

Notes:

(1) NA = No sample taken or no sample analyzed.
U = Not detected at detection limit.
< = Not detected at detection limit.

6.1.7 Stack Gases Analysis

Gas sampling was conducted during all validation test runs at the Axi-Shear exhaust duct, sampling point SP-2. Summaries of the stack gas analyses are shown in Table 6-8 and Table 6-9, which show parameter concentrations and mass emission rates respectively.

Stack gases were continuously monitored (CEM) during all test runs for oxygen, carbon dioxide, sulfur dioxide, nitrogen oxides, carbon monoxide and nitrous oxide. Gas samples were also collected from the same location via sampling trains and analyzed for volatile organic compounds (VOC, Method 8260C), semi-volatile organic compounds (SVOCs, Method 8270C), and depending on feed, halogens and specific organic compounds. Stack gas flow rates were also measured however, the accuracy of these measurements are questionable and have been adjusted as per discussion in Section 6.4.2. Corrected averages of the CEM parameters for each validation test runs are included in Table 6-8 and Table 6-9.

The heaviest concentration of VOC emissions occurred during the HD neutralent simulant runs. The maximum Total VOC emissions were measured in run H-3 with a concentration of 172 mg/m^3 and an emission rate of 0.047 lb/hr. In run H-3, 1,2-dichloroethane represented approximately 96 wt% of the reported Total VOCs (0.045 lb/hr).

SVOC are generally emitted at higher concentrations in the GB neutralent simulant runs than in the HD neutralent simulant runs. A sum of all reported SVOCs equated to a maximum total concentration (G-4) of 0.061 mg/dscf with a corresponding emission rate of 0.00057 lb/hr. In this case, 63% of the total SVOCs are represented by benzoic acid.

Table 6-8 Stack Gas Analyses (Concentrations)

Sample Location		SP-02	SP-02	SP-02	SP-02	SP-02	SP-02	SP-02	SP-02
Sample Description		Stack Gas	Stack Gas	Stack Gas	Stack Gas	Stack Gas	Stack Gas	Stack Gas	Stack Gas
Run Number		H-2	H-3	H-4	H-4	G-2	G-3	G-4	G-4
Run Hour	Units	0-8	0-8	0-8	16-24	0-8	0-8	0-8	16-24
Date of Sample		05/23/01	05/30/01	05/24/01	05/25/01	06/04/01	06/05/01	06/01/01	06/02/01
VOC - GAS									
Acetone	µg/m^3	NA	<34	<48	<48	NA	<10	266	<14
Benzene	µg/m^3	NA	75	166	<65	NA	<13	<97	<19
Bromomethane	µg/m^3	NA	<83	1,106	<118	NA	<24	<178	<36
Chloroform	µg/m^3	NA	1,837	17,877	13,408	NA	160	990	417
Chloromethane	µg/m^3	NA	1,365	<42	3,780	NA	<8	<63	<13
1,2-Dichloroethane	µg/m^3	NA	164,659	38,695	9,880	NA	<16	659	37
Dichloromethane	µg/m^3	NA	919	4,946	3,533	NA	276	353	145
cis-1,3-Dichloropropene	µg/m^3	NA	<65	<92	<92	NA	<18	40	<28
Ethanol	µg/m^3	NA	<307	<441	55,575	NA	<88	<662	<132
Hexane	µg/m^3	NA	208	1,183	1,040	NA	79	222	65
1,1,2-Trichloroethane	µg/m^3	NA	122	283	261	NA	<22	<166	<33
Toluene	µg/m^3	NA	<54	<77	<77	NA	23	<115	<23
Vinyl Chloride	µg/m^3	NA	2,574	<52	<52	NA	<10	<78	<16
Total	µg/m^3		171,759	64,256	87,476	NA	538	2,530	664
SVOC - GAS									
1,2,4-Trichlorobenzene	µg/dscf	0.32	0.26	0.29	0.34	0.18	0.13	<0.74	<0.77
1,2-Dichlorobenzene	µg/dscf	0.08	0.09	0.12	0.08	<0.07	<0.08	<0.74	<0.77
2,4-Dinitrophenol	µg/dscf	<0.017	0.24	<0.19	<0.16	0.51	2.31	7.78	15.38
2-Nitrophenol	µg/dscf	0.88	1.85	0.61	0.84	1.86	9.09	5.19	6.92
4-Nitrophenol	µg/dscf	0.78	1.93	0.57	0.81	1.46	5.30	<0.52	<0.54
Benzoic acid	µg/dscf	19.45	23.36	17.00	13.82	19.36	37.88	28.90	38.45
Benzyl butyl phthalate	µg/dscf	0.03	0.03	<0.02	<0.02	0.03	0.03	<0.22	<0.23
Bis(2-ethylhexyl)phthalate	µg/dscf	0.25	<0.05	<0.06	<0.05	<0.05	<0.05	<0.52	<0.54
Diethyl phthalate	µg/dscf	0.11	<0.04	<0.04	<0.04	<0.04	<0.04	<0.41	<0.42
Di-n-butyl phthalate	µg/dscf	0.05	<0.04	<0.04	<0.04	<0.04	<0.04	<0.41	<0.42
Naphthalene	µg/dscf	<0.01	0.02	0.03	<0.01	<0.01	<0.01	<0.11	<0.12
Phenol	µg/dscf	0.60	1.04	0.53	0.51	0.58	<0.04	<0.41	<0.42
Total	µg/dscf	22.57	28.82	19.14	16.39	23.99	54.76	41.87	60.76
MISCELLANEOUS - GAS									
HCl	µg/dscf	30	44	44	35	NA	NA	NA	NA
Chlorine	µg/dscf	51	182	159	124	NA	NA	NA	NA
HF	µg/dscf	NA	NA	NA	NA	NA	<0.27	<0.27	<0.27
MEA	µg/dscf	<7.6	<8.1	<7.5	<9.6	NA	NA	<8.6	<9.1
DMSO	µg/dscf	<69609	<77255	<83379	<76128	NA	NA	NA	NA
DMMP	µg/dscf	NA	NA	NA	NA	<1.5	<4.2	<1.5	<1.5
CEM - GAS									
O_2	%	20.16	20.1	20.27	20.1	20.6	20.77	20.53	20.56
CO_2	%	0.67	0.57	0.71	0.84	0.56	0.49	0.55	0.67
SO_2	ppmdv	11.02	10.31	7.67	8.91	19.41	22.25	21.36	30.23
NO_x	ppmdv	639	411	535	673	459	266	454	486
CO	ppmdv	68.4	67.4	108	156.7	98.4	101.1	75.2	95.8
THC (Total Hydrocarbons-CH4)	ppmdv	114.18	151.79	137.4	177.21	54.81	52.45	32	54.95
N_2O	ppmdv	42.21	33.79	59.6	93.55	32.23	34.21	12.18	51.26

Notes:

(1) NA = No sample take or analyses performed.
< = Undetected at detection limit.

(2) dscf = Dry Standard Cubic Feed (Standard is defined at 1 atmosphere pressure at 68°F). ppmdv = parts per milllion-dry volume.

Table 6-9 Stack Gas Analyses (Emission Rates)

Sample Location		SP-02	SP-02	SP-02	SP-02	SP-02	SP-02	SP-02	SP-02
Sample Description		Stack Gas	Stack Gas	Stack Gas	Stack Gas	Stack Gas	Stack Gas	Stack Gas	Stack Gas
Run Number		H-2	H-3	H-4	H-4	G-2	G-3	G-4	G-4
Run Hour	Units	0-8	0-8	0-8	16-24	0-8	0-8	0-8	16-24
Date of Sample		05/23/01	05/30/01	05/24/01	05/25/01	06/04/01	06/05/01	06/01/01	06/02/01
VOC EMISSION RATES									
Flow rate (Adjusted)[2]	dscf	73	73	73	73	71	71	71	71
Flow rate (measured)[2]	dscf	154	155	157	158	156	157	155	156
Acetone	lb/hr	NA	<9.23E-06	<1.32E-05	<1.32E-05	NA	<2.57E-06	7.07E-05	<3.85E-06
Benzene	lb/hr	NA	2.04E-05	4.53E-05	<1.78E-05	NA	<3.46E-06	<2.59E-05	<5.19E-06
Bromomethane	lb/hr	NA	<2.27E-05	3.02E-04	<3.24E-05	NA	<6029E-06	<4.72E-05	<9.47E-06
Chloroform	lb/hr	NA	5.03E-04	4.89E-03	3.67E-03	NA	4.26E-05	2.63E-04	1.11E-04
Chloromethane	lb/hr	NA	3.73E-04	<1.15E-02	1.03E-03	NA	<2.23E-06	<1.68E-05	<3.35E-06
1,2-Dichloroethane	lb/hr	NA	4.50E-02	1.06E-02	2.70E-03	NA	<4.26E-06	1.75E-04	9.85E-06
Dichloromethane	lb/hr	NA	2.51E-04	1.35E-03	9.66E-04	NA	7.33E-05	9.40E-05	3.85E-05
cis-1,3-Dichloropropene	lb/hr	NA	<1.77E-05	<2.52E-05	<5.46E-05	NA	<4.93E-06	1.06E-05	<7.37E-06
Ethanol	lb/hr	NA	<8.38E-06	<1.20E-04	1.52E-02	NA	<2.354E-05	<1.76E-04	<3.52E-05
Hexane	lb/hr	NA	5.69E-05	3.24E-04	2.84E-04	NA	2.10E-05	5.91E-05	1.72E-05
1,1,2-Trichloroethane	lb/hr	NA	3.34E-05	7.74E-05	7.13E-05	NA	<5.921E-06	<4.43E-05	<8.88E-06
Toluene	lb/hr	NA	<1.47E-05	<2.10E-05	<2.10E-05	NA	6.22E-06	<3.06E-05	<6.10E-06
Vinyl Chloride	lb/hr	NA	7.04E-04	<1.42E-05	<1.42E-05	NA	<2.77E-06	<2.08E-05	<4.15E-06
Total	lb/hr		4.70E-02	1.76E-02	2.39E-02		1.43E-04	6.73E-04	1.77E-04
SVOC EMISSION RATES									
1,2,4-Trichlorobenzene	lb/hr	3.11E-06	2.47E-06	2.81E-06	3.25E-06	1.68E-06	1.25E-06	<6.96E-06	<7.24E-06
1,2-Dichlorobenzene	lb/hr	8.20E-07	8.59E-07	1.17E-06	7.81E-07	<6.87E-07	<7.10E-07	<6.96E-06	<7.24E-06
2,4-Dinitrophenol	lb/hr	<1.64E-06	2.36E-06	<1.87E-06	<1.56E-06	4.80E-06	2.17E-05	7.31E-05	1.44E-04
2-Nitrophenol	lb/hr	8.54E-06	1.79E-05	5.86E-06	8.14E-06	1.75E-05	8.54E-05	4.87E-05	6.50E-05
4-Nitrophenol	lb/hr	7.52E-06	1.86E-05	5.47E-06	7.81E-06	1.37E-05	4.98E-05	<4.86E-06	<5.05E-06
Benzoic acid	lb/hr	1.88E-04	2.26E-04	1.64E-04	1.33E-04	1.82E-04	3.56E-04	2.71E-04	3.61E-04
Benzyl butyl phthalate	lb/hr	2.60E-07	3.33E-07	<2.34E-07	<1.95E-07	2.64E-07	3.17E-07	<2.09E-06	<2.17E-06
Bis(2-ethylhexyl)phthalate	lb/hr	2.46E-06	<4.99E-07	<5.49E-07	<4.56E-07	<4.82E-07	<4.79E-07	<4.86E-06	<5.05E-06
Diethyl phthalate	lb/hr	1.09E-06	<3.94E-07	<4.30E-07	<3.58E-07	<3.77E-07	<3.19E-07	<3.83E-06	<3.97E-06
Di-n-butyl phthalate	lb/hr	5.12E-07	<3.94E-07	<4.30E-07	<3.58E-07	<3.77E-07	<3.19E-07	<3.83E-06	<3.97E-06
Naphthalene	lb/hr	<1.02E-07	1.86E-07	2.93E-07	9.75E-08	<1.03E-07	<1.07E-07	<1.04E-06	<1.08E-06
Phenol	lb/hr	5.81E-06	1.00E-05	5.08E-06	4.88E-06	5.49E-06	<3.91E-07	<3.83E-06	<3.97E-06
Total	lb/hr	2.18E-04	2.78E-04	1.85E-04	1.58E-04	2.25E-04	5.14E-04	3.93E-04	5.71E-04
MISCELLANEOUS GAS EMISSION RATES									
HCl	lb/hr	2.93E-04	4.26E-04	4.24E-04	3.38E-04	NA	NA	NA	NA
Chlorine	lb/hr	4.98E-04	1.76E-03	1.52E-03	1.21E-03	NA	NA	NA	NA
HF	lb/hr	NA	NA	NA	NA	NA	<2.85E-06	<2.59E-06	<2.49E-06
MEA	lb/hr	<7.44E-05	<7.77E-05	<7.11E-05	<9.33E-05	NA	NA	<8.15E-05	<8.47E-05
DMSO	lb/hr	<0.66	<0.75	<0.79	<0.74	NA	NA	NA	NA
DMMP	lb/hr	NA	NA	NA	NA	<1.40E-05	<4.02E-05	<1.42E-05	<1.42E-05
CEM EMISSION RATES									
SO_2	lb/hr	8.01E-03	7.49E-03	5.58E-03	6.47E-03	1.37E-02	1.57E-02	1.51E-02	2.14E-02
NO_x	lb/hr	3.34E-01	2.15E-01	2.79E-01	3.52E-01	2.33E-01	1.35E-01	2.31E-01	2.47E-01
CO	lb/hr	2.18E-02	2.14E-02	3.44E-02	4.99E-02	3.04E-02	3.13E-02	2.33E-02	2.96E-02
THC (Total Hydrocarbons-CH4)	lb/hr	2.08E-02	2.76E-02	2.50E-02	3.23E-02	9.69E-03	9.32E-03	5.68E-03	9.74E-03
N_2O	lb/hr	2.11E-02	1.69E-02	2.98E-02	4.67E-02	1.57E-02	1.66E-02	5.91E-03	2.49E-02

Notes:

(1) NA = No sample take or analyses performed.
U = Undetected at detection limit.
< = Undetected at detection limit.

(2) Measured flow rates are adjusted to match expected flow (Section 6.4.2) and to account for inaccurate flow measurement. Emission rate reflect adjusted flow rate.

(3) dscf = Dry Standard Cubic Feed (Standard is defined at 1 atmosphere pressure at 68°F ppmdv = parts per milllion-dry volume

6.1.8 Electrolytes Analyses

The electrolytes (anolyte and catholyte) are process fluids, which are used during the destruction of organic materials. Many organic wastes contain inorganic elements (Al, As, Ca, Cu, F, Fe, Pb, Mg, Ni, P, K, Na, S, Zn) which will not be treated by the CerOx process but rather be retained in the anolyte solution as soluble or insoluble salts.[25] Eventually, these salts reduce the effectiveness of the unit to a point where the anolyte solution must be replaced. The catholyte solution will also need replacement based on the build-up of contaminants. Contaminants in the catholyte include components that pass through the Nafion membrane (separates anolyte from catholyte in the electrochemical cells) and the accumulation of metals and suspended solids from the make-up of nitric acid. The electrolytes eventually become spent and become process wastes.

During testing the anolyte and catholyte solutions were replaced with fresh solutions at the beginning of the series of HD neutralent simulant runs and the beginning of the series of GB neutralent simulant runs. Summaries of the anolyte and catholyte analyses are provided in Table 6-10 and Table 6-11 respectively.

6.1.8.1 Anolyte analyses

Figure 6-1 shows a typical anolyte sample, which was collected and transferred to sample containers. 1,2-dichloroethane, being a feed material of the HD neutralent simulant, was only detected in the anolyte solution during run H-4 at levels, which ranged from 0.07 and 6.8 mg/L.

Figure 6-1 Anolyte Samples

DMSO was detected in run H-3 at 3700 mg/L. This represents approximately 1.5 kg of DMSO in the anolyte solution (initial charge of 110 gallons) and nearly 90 wt% of the DMSO which was fed (based on expected simulant feed compositions) to the unit in all of HD neutralent simulant runs combined. This would appear to be quite a high concentration in the anolyte and is not supported by a reported build up of DMSO in the chronological progression of analyzed samples.

MEA was reported at below detection limits in all runs except for H-4 where no sample was analyzed.

Bromomethane and chloromethane were also reported in the final anolyte solutions except for H-3 which had no sample analyzed. These components were also detected in the nitric acid used to make the anolyte solution (see Table 6-5).

The anolyte solution for the GB neutralent simulants runs reported 0.3 and 0.22 mg/L DMMP (a feed material) in runs G-2 and G-3 respectively. Assuming a concentration of 0.3 mg/L DMMP in the anolyte solution, the total amount of DMMP in the anolyte would equate to less than 0.001 wt% of the DMMP that was fed (based on expected concentrations in the simulants) to the CerOx System 2 during the entire GB neutralent simulant campaign.

Concentration of Ce were reported in all of the anolyte solutions and ranged from 52,000 to 210,000 mg/L. This represents a range of 0.4 to 1.5 M total cerium. The initial total cerium concentration in the anolyte was 1.5 M.

Table 6-10 Anolyte Analyses

Sample Location		SP-10	SP-10	SP-10	SP-10	SP-10	SP-10	SP-10	SP-10	SP-10
Sample Description		Anolyte	Anolyte	Anolyte	Anolyte	Anolyte	Anolyte	Anolyte	Anolyte	Anolyte
Run Number		H-2	H-3	H-4	H-4	H-4	G-2	G-3	G-4	G-4
Run Hour	Units	0	8	0	8	24	8	8	0	24
Date of Sample		05/23/01	05/30/01	05/24/01	05/25/01	05/25/01	06/04/01	06/05/01	06/01/01	06/02/01
INORGANIC AND MISCELLANEOUS										
Aluminum	mg/L	1700	1200	1400	130	1400	1100	1200	1,200	1,100
Cerium	mg/L	210,000	150,000	160,000	120,000	160,000	130,000	110,000	52,000	120,000
Chromium	mg/L	3.5	84	42	9	85	31	45	3.6	20
Copper	mg/L	<8.9	1	<4.2	<0.06	<3.2	<5.6	<5.7	<5.7	<3.8
Iron	mg/L	110	480	320	51	440	150	200	34	97
Mercury	mg/L	8.4	35	9.4	0.051	23	15	16	0.013	0.017
Zinc	mg/L	<1.0	3	1.5	<1	2	1.2	1.1	<1	<1.0
pH		NA	NA	NA	NA	NA	NA	NA	NA	NA
TSS	mg/L	600	640	710	630	800	1400	570	420	810
TIC	mg/L	<10	NA	<100	<100	27	25	26	17	21
TOC	mg/L	7.3	NA	980	2000	1800	1600	1800	20	1700
Chloride	mg/L	NA	NA	99	96	120	NA	NA	NA	NA
Fluoride	mg/L	NA	NA	NA	NA	NA	1200	1300	47	<50
ortho-Phosphate (as P)	mg/L	570	100	NA	NA	NA	<100	<100	<100	<100
Sulfate (as SO4)	mg/L	<100	<100	<100	120	140	NA	NA	NA	NA
VOC - LIQUID										
Benzene	µg/L	<2.5	NA	<50	<50	<50	<50	<50	<50	<50
Bromomethane	µg/L	46	NA	440	450	120	180	<100	<100	<100
Chloroform	µg/L	28	NA	<40	<40	<40	<40	<40	<40	<40
Chloromethane	µg/L	44	NA	1100	2100	1400	<140	<140	<140	<140
1,2-Dichloroethane	µg/L	<2.0	NA	500	6800	70	<40	<40	80	<40
Methylene Chloride	µg/L	<12	NA	<230	<230	<230	<230	<230	<230	<230
Total	µg/L	118	NA	2040	9350	1590	180	0	80	0
SVOC - LIQUID										
2,6-Dinitrotoluene	µg/L	<0.6	<6.0	<2.5	<23.0	<6	<6.0	<6.0	180	<6.0
Benzoic acid	µg/L	60	<50	<25	<25	<50	<50	<50	<50	<50
N-Nitrosodimethylamine	µg/L	<10	<100	<50	<50	<100	<100	<100	<100	<100
MEA - LIQUID										
MEA - Ethanolamine	mg/L	NA	<0.2	<0.2	<0.2	<0.002	<0.002	<0.002	<200	<200
Schedule 2										
DMSO	?g/µL	1000 U	3700	1000 U	NA	1000 U	1000 U	NA	NA	NA
DMMP	µg/L	NA	NA	NA	NA	NA	300	220	20 U	20 U

Notes:

(1) The EMPA results include IMPA & MMP, which coelute with EMPA.
(2) NA = No sample taken or no sample analyzed.
U = Undetected at detection limit.
< = Undetedted at detection limit.

6.1.8.2 Catholyte Analyses

The catholyte solution in the HD neutralent simulant runs suggested trends where the following components increased in concentration as the runs were completed: aluminum, cerium, chromium, iron, mercury, zinc, TOC, and sulfate. Although the increase in metals (excluding cerium) could be due to the corrosion of equipment, a more likely source is the metals, which are fed to the catholyte via the nitric acid make-up to the system. The increase in cerium suggests that the cerium is being transferred across the Nafion membrane or there is a leak somewhere in the electrochemical cells. CerOx believes that the leakage of cerium from the anolyte to the catholyte occurred through some internal leakage path in the cellpacks that could be the result of insufficient weld time[26]. The concentration of cerium in the catholyte ranges from 60,000 to 270,000 mg/L.

In both the HD and GB neutralent simulant runs the concentration of TOC in the catholyte solution had an increasing trend. This indicates that organic material is accumulating in the catholyte solution from the anolyte system through the same leakage path as described above for cerium.

1,2-dichloroethane and DMSO, which are feed materials in the HD simulant neutralent, are reported in the H-4 run analyses. No trend can be seen for the DMSO since only one hit above the detection limit was reported at 1900 mg/L. The 1,2-dichloroethane seems to be trending higher and is found in the final HD neutralent simulant test campaign at 0.084 mg/L.

The total VOCs in the HD neutralent simulant runs ranged from 0.15 to 1.3 mg/L. Of the 1.3 mg/L total VOCs reported in run H-2, 98 wt% was due to Acetone. There is no explanation of why acetone shows up only once in the catholyte solution analyses.

The total VOCs in the GB neutralent simulant runs were generally higher than the HD neutralent simulant runs and ranged between 0.9 to 3.3 mg/L. SVOCs were undetected in the HD neutralent simulant runs and N-Nitroso-dimethylamine showed a steady increase from 2.7 to 4.9 mg/L in the GB neutralent simulant runs. No explanation for the mechanism to form N-Nitroso-dimethylamine or the increasing trend is available at this time.

MEA analyses for both campaigns fell below the detection limits.

DMMP in the GB neutralent simulant runs was reported at <0.02 mg/L before the initial run and 0.15 mg/L following the final run. This suggests that DMMP was passing from the anolyte solution, through the suspected leakage path in the cellpacks, and into the catholyte solution.

Table 6-11 Catholyte Analyses

Sample Location		SP-12	SP-12	SP-12	SP-12	SP-12	SP-12	SP-12	SP-12
Sample Description		Catholyte	Catholyte	Catholyte	Catholyte	Catholyte	Cathloyte	Catholyte	Catholyte
Run Number		H-2	H-3	H-4	H-4	G-2	G-3	G-4	G-4
Run Hour	Units	0	8	0	24	8	8	0	24
Date of Sample		05/23/01	05/30/01	05/24/01	05/25/01	06/04/01	06/05/01	06/01/01	06/02/01
INORGANIC AND MISCELLANEOUS									
Aluminum	mg/L	630	1300	1400	1200	1200	1200	1000	1200
Cerium	mg/L	60,000	120,000	110,000	100,000	99,000	100,000	270,000	110,000
Chromium	mg/L	12	66	35	59	34	46	6.4	24
Copper	mg/L	<3.4	<3.7	<7.1	<3.3	<7.4	<6.5	<2.7	<7.0
Iron	mg/L	260	620	440	650	200	260	45	140
Mercury	mg/L	0.008	0.09	0.021	0.11	0.026	0.028	<0.0025	0.027
Zinc	mg/L	<1.0	3.6	2.2	4.3	1.6	1.8	<1	1.4
pH		NA	NA	NA	NA	1	1	<1	
TSS	mg/L	NA	470	340	280	2500	420	180	250
TIC	mg/L	<100	<12	<10	<10	18	26	17	<10
TOC	mg/L	<0.20	940	540	1100	1400	1600	0.41	1200
Chloride	mg/L	NA	120	180	120	NA	NA	NA	NA
Fluoride	mg/L	NA	NA	NA	NA	980	1100	240	880
ortho-Phosphate (as P)	mg/L	NA	NA	NA	NA	<100	<100	<100	<100
Sulfate (as SO4)	mg/L	NA	290	130	330	NA	NA	NA	NA
VOC - LIQUID									
Acetone	µg/L	1300	<130	<130	<130	<640	<640	<250	<320
Acrolein	µg/L	<10	<51	<51	<51	<260	<260	250	<130
Benzene	µg/L	<1.0	7.1	8.6	<5.0	<25	<25	<10	<13
Bromomethane	µg/L	<2.0	86	73	68	1900	2400	1200	670
Chloroform	µg/L	3.5	15	21	4.3	<20	<20	<8.0	<10
Chloromethane	µg/L	11	250	190	51	740	920	1200	210
1,2-Dichloroethane	µg/L	<0.8	84	6.3	<4.0	<20	<20	12	<10
Methylene Chloride	µg/L	8.2	<23	<23	30	<120	<120	<46	<58
Total	µg/L	1323	442.1	298.9	153.3	2640	3320	2412	880
SVOC - LIQUID									
2,6-Dinitrotoluene	µg/L	NA	<30	<30	<30	<30	<30	NA	<30
Benzoic acid	µg/L	NA	<250	<250	<250	<250	<250	NA	<250
N-Nitrosodimethylamine	µg/L	NA	<500	<500	<500	4000	4900	NA	2700
MEA - LIQUID									
MEA - Ethanolamine	mg/L	NA	<200	<200	<200	<200	NA	<2.0	<200
Schedule 2									
DMSO	?g/µL	NA	1000 U	1000 U	1900	1000 U	NA	NA	NA
DMMP	µg/L	NA	NA	NA	NA	340	150	20 U	120
Comments									

Notes:
(1) NA = No sample taken or no sample analyzed.
U = Undetected at detection limit.
< = Undetected at detection limit.

6.1.9 NOx Caustic Scrubber Liquid

The NOx Caustic Scrubber solution was periodically partially or completely drained to a waste drum. Analyses were performed characterize the solution and determine accumulation of components. Table 6-12 shows the summary of analyses performed.

During the HD neutralent simulant runs, chloride was reported in the scrubber solution and ranged from 280 to 1000 mg/L. This may be construed as evidence for chlorine recovered from the oxidation of 1,2-dichloroethane, but is complicated by the reported analysis of 7100 mg/L chloride in the caustic make-up solution (see Table 6-5). Sulfate was only reported in run H-4 at 1200 mg/L. No other reports of sulfate leads to an uncertainty of its validity. VOCs are reported in relatively low concentrations with a maximum reported during run H-3 of 0.39 mg/L. No 1,2-dichloroethane or DMSO (feed components) were reported in the scrubber solution for HD neutralent simulant runs.

In the GB neutralent simulant runs, there was one reported value for fluoride in the G-3 run of 17 mg/L. The only detected VOC and SVOC parameters were bromomethane (0.44 mg/L) and bis (2-ethylhexyl) phthalate (0.03 mg/L) respectively.

DMMP was detected in the caustic scrubber solution on run G-3 at 0.095 mg/L. This is consistent with DMMP reported in the scrubber effluent analysis for the same run (see Table 6-7).

MEA was not detected above its detection limit in any runs.

Table 6-12 NOx Scrubber Liquid Analyses

Run Number		H-3	H-4	H-4	G-3	G-4
Run Hour	Units	8	0	24	8	24
Date of Sample		05/30/01	05/24/01	05/25/01	06/05/01	06/01/01
INORGANIC AND MISCELLANEOUS						
Aluminum	mg/L	0.45	0.41	0.69	<0.3	<0.3
Cerium	mg/L	0.073	<0.01	4.3	0.058	1.7
Chromium	mg/L	0.21	0.19	0.2	0.23	0.22
Copper	mg/L	<0.06	<0.06	<0.06	<0.06	<0.06
Iron	mg/L	1.9	1.7	1	3.4	1.9
Mercury	mg/L	<0.0025	<0.0025	<0.0025	<0.0025	0.071
Zinc	mg/L	0.11	0.43	0.27	0.14	0.24
pH		13.62	12.27	13.12	13.05	13.15
TSS	mg/L	380	170	270	660	1500
TIC	mg/L	2500	380	4500	3500	6500
TOC	mg/L	54	23	34	10	160
Chloride	mg/L	330	1000	280	NA	NA
Fluoride	mg/L	NA	NA	<15	17	<15
ortho-Phosphate (as P)	mg/L	NA	NA	NA	<100	<100
Sulfate (as SO4)	mg/L	<100	1200	<100	NA	NA
VOC - LIQUID						
Acrolein	µg/L	300	NA	69	<1300	<1300
Bromomethane	µg/L	85	NA	100	<250	440
1,2-Dichloroethane	µg/L	<20	<100	<4.0	<100	<100
Vinyl Chloride	µg/L	<45	NA	41	<230	<230
SVOC - LIQUID						
Bis(2-ethylhexyl)phthalate	µg/L	<2.8	<2.8	5.4	33	<14
Nitrobenzene	µg/L	<4.0	<4.0	3.4	<20	<20
MEA - LIQUID						
MEA - Ethanolamine	mg/L	<0.2	<0.2	<0.2	<2000	<2000
Schedule 2						
DMSO	?g/µL	1000 U	1000 U	1000 U	NA	NA
DMMP	µg/L	NA	NA	NA	95	20 U
Comments						

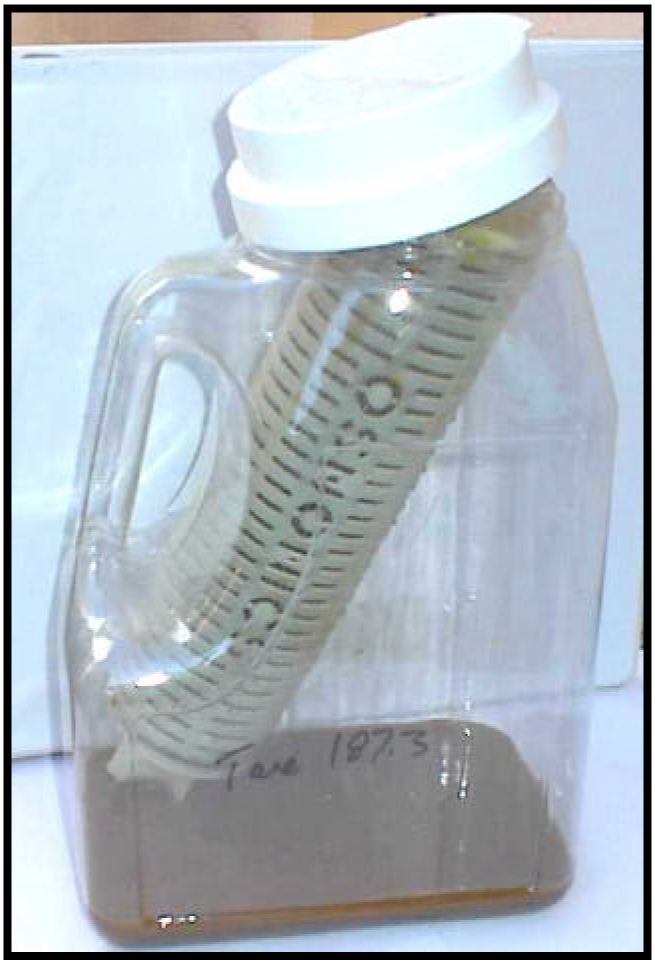
Notes:
(1) NA = No sample taken or no sample analyzed.
U = Undetected at detection limit.
< = Undetected at detection limit.

6.1.10 Anolyte Solids Analyses

The anolyte solids analyses shown below in Table 6-13. The quantity of solids was undetermined do to the complications associated with supplying filter samples to multiple laboratories for analysis and the fact that so little solids were generated. CerOx estimated the total solids generated at less than a couple of grams.

Figure 6-2 shows a typical anolyte filter sample along with residual liquid.

Figure 6-2 Typical Anolyte Filter and Drained Liquid



Aluminum, cerium, chromium and iron were detected in the solid residuals from the HD neutralent simulant runs. In addition to the above metals, mercury and zinc were found in the GB neutralent simulant runs.

DMMP was reported in G-4 at 29 ug/kg. Phosphate was also reported in the GB neutralent simulant runs with concentrations ranging from 32 to 55 mg/kg.

TCLP analyses could not be performed due to insufficient sample quantities.

Table 6-13 Anolyte Solids Analyses

Run Number / Date of Sample		H-2 05/23/01	H-3 05/30/01	H-4 05/25/01	G-2 06/04/01	G-3 06/05/01	G-4 06/02/01
SOLIDS ANALYSES							
Aluminum	mg/kg	720	NA	553	848	2605	1286
Cerium	mg/kg	59347	NA	56446	61114	196609	92256
Chromium	mg/kg	301	NA	1646	117	79	62
Copper	mg/kg	<79	NA	<82	<87	<413	<137
Iron	mg/kg	3165	NA	4763	394	836	531
Mercury	mg/kg	<0.04	NA	<0.03	0.12	0.39	0.34
Zinc	mg/kg	<20	NA	<15	<1.0	32	18
Schedule 2							
DMSO	mg/kg	1800	2500	2700	1250 U	NA	1250 U
DMMP	µg/kg	NA	NA	NA	8 U	10 U	29
Phosphate	mg/kg	NA	NA	NA	35.1	55.4	32.3
Comments							

Notes:

(1) NA = No sample taken or no sample analyzed.
U = Undetected at detection limit.
< = Undetected at detection limit.

(2) TCLP analysis not performed due to insufficient sample.

6.2 Effluent Evaluation

6.2.1 Scrubber Effluent Evaluation

Based on the LEST results, scrubber effluent generated by a CerOx system treating HD neutralent and GB neutralent should require minimal, if any, treatment before it could be discharged to a wastewater treatment facility. This conclusion is consistent with the existing operating permit of the CerOx System 2 at UNR that allows discharges to the City of Reno publicly owned treatment works (POTW). The analytical results for the HD and GB neutralent simulant test runs are show in Table 6-6 and Table 6-7 respectively.

A primary evaluation criteria for determining the viability of disposing of scrubber effluent (Axi-Shear Scrubber discharge) generated during operation of the CerOx system is a limit of 25 ppm on TOC. This value is based on the existing TOC concentration permitted in wastewater discharged from the Pine Bluff Arsenal Central Waste Treatment facility to the Arkansas River, and is therefore a conservative evaluation criteria. It is expected that scrubber effluent from a CerOx treatment system or any neutralent post-treatment technology would be discharged to a wastewater treatment facility before ultimate disposal. The 25 ppm criteria provide a broad evaluation of the viability of disposing of the scrubber effluent. TOC measured in samples from the HD neutralent simulant validation test runs ranged from 2.0 – 25 mg/L. The 25 mg/L represented the starting value of the first HD neutralent simulant validation test is also a representation of the effluent generated in the work-up run. The next highest TOC concentration was reported at 5.2 mg/L.

Samples from the GB neutralent simulant test runs contained TOC ranging from 1.6 - 56 mg/L. The TOC values reported for the G-3 run at hours 4 and 8 (56 and 55 mg/L respectively) are suspect and do not compare well with other samples with respect to their level of corresponding VOCs and SVOCs data.

Ignoring these samples, the highest TOC reported was 6.3 mg/L. Thus, scrubber effluent generated over the course of CerOx treatability testing fell well below the target criteria for acceptable discharge.

The pH of the scrubber effluent during both HD neutralent simulant and GB neutralent simulant test runs ran consistently between 8.0 and 9.0 according to continuous process monitoring data collected by CerOx. Laboratory pH analysis ranged from 8.09 - 9.63 for HD neutralent simulant test run samples and from 9.26 - 11.96 for GB neutralent simulant test run samples. The differences in pH range may reflect pH changes resulting from sample degradation withholding time or variance in field or laboratory pH probe calibration. Discharge pH requirements may vary with location based on local wastewater treatment facility influent characteristics, or receiving water conditions, but typically require a range of 6.0 - 9.0. Closer attention to scrubber effluent pH and/or addition of pH adjustment may be necessary in an operating CerOx system treating NSCMP wastes.

The total VOCs detected in all scrubber effluent samples during the HD neutralent simulant tests amounted to less than 2 mg/L and less than 0.11 mg/L in the GB neutralent simulant test runs. Individual VOCs detected in all scrubber effluent samples were reported in the low µg/L range, with the exception of 1,2-dichloroethane in the H-2 and H-3 runs which ranged from 0.69 to 1.9 mg/L. These concentrations of 1,2-dichloroethane are of regulatory concern because the material is regulated as a toxic contaminant under the Toxicity Characteristic Leaching Procedure (TCLP) at a concentration of 0.5 ppm (DO28 waste; see 40 CFR 261.24). Although several samples during the H-2 and H-3 test runs exceeded this level, most samples were well below the regulatory level. If CerOx scrubber effluent consistently exceeded this level, disposal options could be restricted due to its classification as a hazardous waste. Note that DCE is a simulant ingredient and not expected to be in the actual NSCMP HD neutralents to be treated and therefore would not be a regulatory concern.

All of the metal concentrations analyzed were below mg/L levels, less than limits typical for most discharges to sewer systems. For direct surface water discharges, concentrations of copper and zinc, and occasionally aluminum, while low, were above EPA Recommended Ambient Freshwater Quality Criteria. Applicable discharge limits would ultimately depend on site-specific receiving-stream loading and flow, total maximum daily loading (TMDL) requirements, discharge flow, and whole effluent toxicity factors.

6.2.2 Stack Gas Evaluation

Emission standards applicable to a specific unit will be a function of the unit's location and size as determined in a case-by-case control technology evaluation under Prevention of Significant Deterioration (PSD), Non-attainment New Source Review, or a state minor source construction permit program. These programs, and subsequent control technology determinations, are triggered based on a source's annual "potential to emit" on a mass emissions basis. In some cases, control technology requirements are established for specific classes of sources based on technology or industry classifications under Federal New Source Performance Standards (NSPS), National

Emissions Standards for Hazardous Air Pollutants (NESHAPs) or pertinent state/local source category standards. Currently, no NSPS or NESHAPs have been established that would apply directly to the CerOx technology. Although clearly not applicable, the NSPS for Commercial and Industrial Solid Waste Incinerators (40 CFR 60, Subpart CCCC) and the NESHAP for Hazardous Waste Combustors (40 CFR 63, Subpart EEE) could be used for a comparative benchmark for CerOx process emissions. Note however, that these standards are intended to serve as basis for comparison between different units of the same technology, rather than direct comparison between technology's performance.

6.2.2.1 NOx Emissions

NOx emissions are of particular interest for the CerOx technology because NOx emissions are strictly regulated in many parts of the country (non-attainment areas) as ozone precursors and because the CerOx process has the potential to generate NOx in significant quantities due to its cathodic reduction of nitric acid. Average CEM measurements of NOx during the CerOx validation test runs ranged from 266 $ppm_{v\,d}$ - 673 $ppm_{v\,d}$, or 0.135 lb/hr - 0.352 lb/hr. Average NOx emissions for the HD neutralent simulant test runs (565 $ppm_{v\,d}$) were approximately 35% higher than the GB neutralent simulant test runs (416 $ppm_{v\,d}$), possibly reflecting the nitrogen content of the HD neutralent simulant but probably due to the maintenance of the caustic solution strength in the NOx Caustic Scrubber Drum which was not consistent from run to run. Proper design and control of a NOx Absorption system and an Alkali Scrubber system would be expected to produce far less NOx emissions.

Under Subpart CCCC, standards, the maximum emission limit for NOx is 388 $ppm_{v\,d}$ (@ 7% O_2). As shown on Table 6-8, NOx emissions during all test runs but one (G-3) exceeded this value (@ ~ 20% O_2). As further comparison, most new boilers and gas turbines are currently limited to emission rates significantly less (as low as 2 $ppm_{v\,d}$ for gas turbines). Thus, the CerOx unit's NOx emissions would appear to be relatively high on a concentration basis. The combination of high emission concentration with low exhaust temperature may also produce a concern for localized elevated ambient NOx concentrations.

On a mass emissions basis, worst case emissions from a System 2 at 8,760 hours per year would constitute a potential emission source of 1.5 tons NOx per year. Except in "extreme" ozone nonattainment areas or at sites with other significant NOx emission sources, a new source of this size would not typically be significant enough to trigger major source permit and control technology requirements. However, a larger CerOx system sized for NSCMP operations would emit proportionally higher amounts of NOx, potentially triggering additional permit and control technology requirements. Additional CerOx process optimization to minimize NOx emissions would help eliminate concerns over high relative

NOx concentrations and minimize the need for potential additional add-on NOx controls.

6.2.2.2 Feedstock Component Stack Gas Emissions

The HD neutralent simulant was made with MEA, 1,2-dichloroethane, DMSO and water. Samples were drawn for analysis of all the components, except for water, to determine effluent characteristics and material balance.

DMSO samples were taken by TRC during processing using midget impingers (ACT Method 013). SwRI was contracted to perform the DMSO analyses. SwRI diluted all liquid samples by 100 in order to protect their equipment from contamination. At these dilutions, all of the DMSO gas samples fell below the calculated detection limit. The detection limit for DMSO under the diluted conditions would only report emissions that were greater than 0.66 to 0.79 lb/hr. Since the maximum feed rate of DMSO to the CerOx System 2 (based on expected concentrations) was only 0.1 lb/hr, the laboratory analysis is meaningless for the calculation of DMSO destruction.

1,2-dichloroethane was reported in the stack gas samples and averaged 165 mg/m^3 for run H-3 and 24.3 mg/m^3 for run H-4 with equivalent mass emission rates of 0.045 to 0.0067 lb/hr respectively. This indicates that run H-3 emitted 38 wt% of the 1,2-dichloroethane feed (based on expected concentrations) and run H-4 emitted 6 wt% of the 1,2-dichloroethane feed (based on expected concentrations).

6.2.2.3 Hydrocarbons and Hazardous Air Pollutants

Volatile organic compound (VOC) emissions are regulated under Federal and state air pollution control programs as ozone precursors. Like NOx, VOC emissions may be restricted by categorical NSPS or "reasonably available control technology" (RACT) standards for specific source categories, but none have been established that would apply directly to the CerOx MEO technology. VOC sources are also subject to the generic PSD/Non-attainment New Source Review permit requirements based on the source's annual "potential to emit" at maximum capacity.

VOC emissions were measured generically as total hydrocarbons (THC) which were monitored continuously during each of the validation test runs. Individual VOC species were also measured concurrently. Continuous THC measurements ranged from 0.021 - 0.032 lb/hr during the HD neutralent simulant test runs and from 0.0057 - 0.0097 lb/hr during the GB neutralent simulant test runs. Individual VOC species measured during test run H-3 totaled 0.047 lb/hr, higher than the CEM THC result (0.028 lb/hr). Even using the 0.047 lb/hr maximum measurement, potential VOC emissions from the CerOx System 2 unit at 8,760 hours per year would total only 412 lb (0.21 tons per year). This level of potential VOC emissions would not be considered significant under Federal regulations, and most state or local regulatory programs.

Note however that much of the VOC emitted during the HD neutralent simulant test runs (and the H-3 test run in particular) was 1,2-dichloroethane - a component of the simulant and not a compound found in the actual NSCMP HD neutralent[27]. As evidenced by the GB neutralent simulant test run data, VOC emissions would otherwise be expected to be substantially lower, and less of a regulatory issue. Also as noted in Section 5.3, CerOx has already implemented modifications to the system's Gas Phase Reactor to improve destruction of volatile components such as 1,2-dichloroethane.

Under the Clean Air Act Amendments of 1990, the U.S. EPA has established standards applicable to emissions of Hazardous Air Pollutants (HAPs). A major HAP source is one that has potential HAP emissions of a single compound greater than 10 tons per year (tpy) or combined HAP emissions greater than 25 tpy. Smaller sources are referred to as area sources. Limits on HAP emissions are established for specific source categories considered Maximum Achievable Control Technology (MACT) based on the characteristics and operations of that category. Although no NESHAP and associated MACT standard has been established that would apply directly to the CerOx MEO technology, MACT standards for hazardous waste combustors are established under Subpart EEE that apply to both major and area sources. The MACT standards require that hazardous waste combustors limit CO concentrations to below 100 ppm_{vd} (@ 7% O_2) or the total concentration of hydrocarbons to below 10 ppm_{vd} (@ 7% O_2). Compliance with these standards generally limits potential HAP emissions, without establishing additional MACT standards for specific organic HAPs.

The THC and CO content of the stack gas was monitored continuously during all validation test runs (see Tables 6-8 and 6-9). The CO concentrations reported ranged from 67.4 - 156.7 ppm_{vd} with most runs below or near the 100 ppm_{vd} level. Note that CO is limited under the Subpart EEE standard as an indicator of complete combustion, and as the CerOx process is not a combustion process, is not directly applicable. CerOx has argued that CO has not been found to be a product of MEO destruction of organic materials during very careful studies performed at Lawrence Livermore National Laboratory which tracked all concentrations of all reactants, reaction intermediates and products.[28] Further investigation on CO concentrations is required.

THC emissions monitored continuously during the test runs ranged from 114.2 - 177.2 ppm_{vd} during the HD neutralent simulant feeds and from 32 - 55.0 ppm_{vd} during the GB neutralent simulant feeds.

During the HD neutralent simulant test runs, THC consisted of primarily 1,2-dichloroethane, chloroform, dichloromethane, and in one test run (H-4, hrs 16-24), ethanol. During the GB neutralent simulant test runs, THC consisted primarily of chloroform and dichloromethane. Each compound (except ethanol) is regulated as a HAP. Ethanol is a simple organic molecule that would not be expected to be present as a breakdown product of the CerOx system, and is most likely due to lab error. HAPs measured in the SVOC analysis were also found, but at extremely low levels. While the CEM THC measurements were all above the 10 ppm_{vd} level required for hazardous waste combustors (Subpart EEE), as noted above, they are collectively well under a 1 ton per year HAP source and individually even less. Further optimization of the CerOx system (i.e., Gas Phase Reactor) should reduce emissions of organic HAPs to even lower levels.

Hydrochloric acid (HCl) and chlorine (Cl_2) are two additional HAPs emitted from the CerOx HD neutralent simulant test runs in significant quantities. The Subpart EEE standard limits HCl and Cl_2 to 21 ppm_{vd} (combined, expressed as HCl equivalents), corrected to 7% O_2. HCl emissions ranged from 651 - 955 ppm_{vd} and Cl_2 emissions ranged from 568 - 2030 ppm_{vd} (uncorrected for O_2).

Although the Subpart EEE standard is clearly not directly applicable to the CerOx technology, the HCl and Cl_2 limit is really function of scrubber efficiency, not the core oxidation technology. The test results suggest that the CerOx scrubber is providing very limited HCl and Cl_2 removal and requires significant improvement. Improved scrubbing technology should be adequate to meet the imposed standards. Mass emissions of HCl and Cl_2 are not high enough to constitute a major HAP source; regulators permitting a NSCMP installation would likely expect significant improvement in HCl and Cl_2 removal efficiency. If HCl and Cl_2 scrubbing efficiency is significantly improved, chloride levels in the wastewater may require additional evaluation.

6.3 Waste Evaluation

6.3.1 Electrolytes Waste Evaluation

Both the anolyte and catholyte solutions are strong nitric acid based materials with pH below the 2.0 criteria constituting a corrosive (D002) hazardous waste upon their replacement. Analyses of both the anolyte and catholyte consistently found chromium levels above the 5.0 mg/l TCLP criteria constituting a toxic (D007) hazardous waste. Analyses of the anolyte solution during the HD neutralent simulant test runs found enough 1,2-dichloroethane in two of five analyses to exceed the TCLP criteria of 0.5 mg/l for a toxic (D028) hazardous waste. Note that the samples of the anolyte solution were taken at EOR. The residual amount of 1,2-dichloroethane, which was present, would be reduced by running the system without organic feed for a period of time to ensure complete reaction of 1,2-dichloroethane and other organics in the anolyte. CerOx commented that it is standard practice to hold any anolyte solution at temperature for at least an hour, without organic additions, before shutting down the system for anolyte changeout[29]. As previously noted, 1,2-dichloroethane is a component of the HD neutralent simulant and not the actual waste material, so would not be expected in NSCMP operation. Other materials that are regulated as contaminants under the toxicity characteristic were present, but at levels below the TCLP criteria.

As a characteristic hazardous waste, the spent electrolyte solutions would have to be recycled/reclaimed or disposed of by a facility permitted under the Resource Conservation and Recovery Act (RCRA) to receive and treat hazardous waste from off-site. As a characteristic hazardous waste, CerOx may have some options to recycle/reclaim the materials either on-site or off-site by taking advantage of potential exemptions. Note however that some states have listed various chemical agents as hazardous waste, and in those states, spent electrolyte solutions could be considered "listed" hazardous waste under the "derived-from" rule [40 CFR 261.3(c)(2)(i)]. In that case, the recycling/reclamation facility would have to be a RCRA-permitted treatment, storage, or disposal facility (TSDF). Although the elevated chromium levels may be present as impurities in the makeup materials or from materials corrosion, its presence could complicate waste management options, particularly disposal. If the electrolytes' only hazardous characteristic is corrosivity (low pH), they can simply be neutralized. However, if regulated for chromium content, additional treatment would be required. Depending on treatment/disposal means, low levels of other contaminants might also become factors relative to RCRA's universal treatment standards (40 CFR 268.48).

6.3.2 NOx Scrubber Solution – Waste Evaluation

The NOx scrubber solution would be considered a corrosive (D002) hazardous waste based on its high pH, typically exceeding the regulatory criteria of 12.5. Although the waste contains several other toxic contaminants regulated as TCLP parameters (chromium, mercury, vinyl chloride), they are not high enough to exceed regulatory criteria. This waste-stream could potentially be neutralized (pH adjusted) under the RCRA wastewater treatment exemption [40 CFR 264.1(g)(6) & 265.1(c)(10)] and discharged if it meets local sewer discharge or surface water discharge standards.

As noted in Section 6.2.1, a principal criteria for NSCMP wastewater disposal is a TOC level at 25 ppm or below. Samples of NOx scrubber solution ranged from a 10 - 160 mg/L TOC, meeting this criteria part of the time. As wastewater from a NSCMP installation would be expected to be discharged to a sewage treatment facility prior to surface water discharge, this waste stream may be acceptable for sewer discharge if TOC levels are maintained in a range which can be effectively treated prior to surface water discharge. Metals concentrations (e.g., aluminum, chromium, iron, zinc) were found at levels similar to limits found in many sewer discharge standards, and above EPA Recommended Ambient Freshwater Quality Criteria. Acceptable levels of metals and other wastewater parameters [total suspended solids (TSS), chloride, and organics] will depend on site-specific factors such as loading in the treatment facility and/or receiving stream, flow and whole effluent toxicity.

Note that the NOx Caustic Scrubber was not originally part of the CerOx System 2. The NOx Caustic Scrubber was added to the system and resides outside of the System 2's footprint. The CerOx System 4, currently being manufactured for UCI, will not have a NOx Caustic Scrubbing system. Instead, CerOx has incorporated an improved NOx Absorption system that will recover more NOx and eliminate the need for the separate NOx Caustic Scrubber system. The tail-gases from the NOx Absorbers will be routed to the Alkali Scrubber, which will be far more efficient than the Axi-Shear Scrubber currently used in UNR's System 2. From the above mentioned improvements, a system built for NSCMP purposes would not have a NOx Caustic Scrubber and therefore would not have to dispose of the spent NOx Caustic Scrubber liquid.

6.3.3 Anolyte Solids Evaluation

Insufficient solids were recovered to conduct complete TCLP testing. A partial metals analysis (mg/kg basis) to characterize the solids recovered are summarized in Table 6-13. The results indicate that the solids contain a significant amount of chromium relative to the TCLP standard of 5.0 mg/l, suggesting that if the chromium is leachable under TCLP test conditions, the solids may constitute a regulated hazardous waste. Total mercury analyses in two samples were also above the TCLP standard of 0.2 mg/l. If the solids are considered regulated hazardous waste, they would also have to meet a TCLP standard for zinc of 4.3 mg/l prior to land disposal under the Universal Treatment Standards (40 CFR 268.48).

6.4 Material Balance

One of the objectives of the LEST of the CerOx Process was to determine an overall material balance. To accomplish this objective, the Test Plan required collection of sufficient data to complete an overall material balance. Table 6-14 shows estimates of the overall feeds, outputs, and wastes for the CerOx LEST. This table shows that the CerOx System 2 processed 57 and 98 kg of HD neutralent simulant and GB neutralent simulant respectively. This equates to an average feed rate of 1.43 kg/hr of HD neutralent simulant and 2.44 kg/hr of GB neutralent simulant. System inputs also included make-up air at 30 acfm, make-up air to the Axi-Shear scrubber (not available at this time), process water to the scrubber, make-up acid to the catholyte system, beginning charge of anolyte, beginning charge of catholyte, and beginning and any additional charges of NOx Scrubber solution.

Outputs from the unit include stack gases and scrubber effluent. Scrubber effluent is generated in the Axi-Shear scrubber, which is made-up with process water. The stack gases exit the Axi-Shear scrubber and remain relatively constant from test to test.

Wastes include the following:

- Anolyte and catholyte solutions were changed between test campaigns per the test plan and did not reflect an operations requirement. Given longer run times, the anolyte and catholyte solutions would eventually be spent and would represent a production waste.
- NOx Caustic Scrubber solution which was removed from the NOx Caustic Scrubber Drum.
- Anolyte filter solids which were found in very low quantities estimated at 2 grams per test run.

Table 6-14 Overall Summary

Test	Units	HD-2	HD-3	HD-4	HD TOTAL	GB-2	GB-3	GB-4	GB TOTAL
Date of Test - 2001		May 23	May 30	May 24-25		June 4	June 5	June 1-2	
Run Time	hrs	8	8	24		8	8	24	
Feeds - Inputs									
Simulant Feeds									
Total Mass	kg	9.74	12.36	34.98	57.08	20.9	19.2	57.6	97.7
Average Flow	kg/hr	1.22	1.55	1.46		2.61	2.40	2.40	
Make-up Air									
NOx Absorber	acfm	30	30	30		30	30	30	
Axi-Shear	acfm	NA	NA	NA		NA	NA	NA	
Process Water									
Flow Rate	gpm	1.6	1	1.6		0.6	0.6	0.6	
Total Flow	gal	768	480	2304	3552	288	288	864	1440
Make-up Acid	kg	50 (est)	49.5	149.5	249	50	50 (est)	142	242
Caustic Solution Make-up									
Axi-Sheer Make-up	gal	6.9	6.9	20.6	34.4	6.9	6.9	20.6	34.4
Outputs									
Wastewater									
Flow Rate	gpm	1.6	1	1.6		0.6	0.6	0.6	
Total Flow	gal	768	480	2304	3552	288	288	864	1440
Stack Gases									
Flow Rate	dscfm	73 (est)	73 (est)	73 (est)		71 (est)	71 (est)	71 (est)	
Total Flow	1000 dscf	35.0	35.0	105.1	175.2	34.1	34.1	102.2	170.4
Wastes									
Electrolyte Solutions									
Anolyte	gal	-	-	110	110	-	-	110	110
Catholyte	gal	-	-	75	75	-	-	75	75
NOx Scrubber Solution	gal	48 (est)	40	52	140	40	40	85	165
Anolyte Filter Solids	g	2 (est)	2 (est)	2 (est)	6	2 (est)	2 (est)	2 (est)	6

Notes:
(1) Value followed by (est) are estimated values.

Some problems were encountered in attempting to close the system material balances. Specific problems are discussed below:

6.4.1 Time to Steady State Conditions[30]

Examination of the temperature and gas composition profiles from the SCADA and CEM systems respectively shows that steady state conditions were not attained for at least two hours into the runs. In particular, anolyte/catholyte temperatures and stack CO2 contents increased rapidly during the first few hours, and clear trends could be seen in other gas compositions as well. Under these circumstances it is difficult, if not impossible, to draw valid conclusions from the data collected during the 8-hour runs. The effect of unsteady state conditions in the 24 hour runs are less and could be assumed to offer better data.

6.4.2 Stack Gas Flow Measurements[31]

Stack gas flow rates, measured by single point pito tube, are reported to be in the range of 154-158 dry standard cubic feet per minute (dscfm). However, if these flow rates are accepted together with the reported stack gas assays for carbon-containing compounds, about twice as much carbon is leaving the system in the stack as was charged in the feed, even assuming there is no significant amount of carbonate in the liquid streams in the process.

It is unlikely that the stack gas CO_2 assays are in error by a factor of two (the CEM and periodic sample assays are in very good agreement); and it is more likely that the reported flow measurements are in error. Single point pito tube measurements cannot integrate flow profiles and are subject to large errors if the tube is misaligned even slightly. Forcing closure of the carbon balance, recognizing the TOC contents of the liquid streams, leads to stack gas flow estimates of 73 and 71 dscfm for HD-4 and GB-4 respectively. Given that these estimates are in substantial agreement strongly suggests that the reported values are overstated.

6.4.3 Solids balances[32]

There is no absolute requirement that the amounts of solids entering and leaving the system be identical, since solids can be created by precipitation reactions or destroyed by dissolution. However, quantifying the amount and characteristics of solids produced is important from an environmental perspective. Therefore, an attempt was made to evaluate the solids balance for the system based on the levels of TSS reported in the various streams and the estimated solids contents of the anolyte filter.

The increase in solids in anolyte plus catholyte plus anolyte filter solids might be interpreted as resulting from precipitation of insoluble cerium salts, which would eventually deplete the system of oxidant. If so, however, it is a very small percentage of the total in the system — of the order of 0.2% — and does not appear to have caused operating problems during these short-term tests. Furthermore the precipitates, if formed, must have been very fine since the filter is estimated to have removed only about 0.5-1% of them.

The decrease in the solids contents of the scrubber streams could be explained by the dissolution of solids brought in with the sodium hydroxide solution in streams of somewhat lower — but still quite high — pH. Alternately, the single sodium hydroxide TSS measurement available could be in error on the high side. None of these materials, except filter solids, were sampled and assayed so their characteristics cannot be determined or their potential environmental impact estimated.

6.4.4 Elemental Balances[33]

It is of great important to establish a closed material balances for both chloride and sulfur in run HD-4 and phosphorous and fluoride in run GB-4, since the information can be used to estimate the extents and mechanisms of destruction of the compounds in the feed that carry them into the system. Unfortunately, it is not possible to do so based on the data obtained in these tests. The problem begins with the assays reported for the neutralent simulants in which neither individual species nor the totals for a class (e.g., TOC) match the values expected based on the recipes used to make up the solutions. Other obvious difficulties arise, as for example, when the NOx scrubber effluent chloride content is roughly an order of magnitude lower than that of the sodium hydroxide charged to it. The results of attempts to close the elemental balances for these runs are summarized in Table 6-15 below.

Table 6-15 Material Balances for Cl, S, P and F

Test Run Element	HD-4 Cl	HD-4 S	GB-4 P	GB-4 F
Input Stream Quantity, g atom				
Feed	27.6	13.5	27.9	26.5
Scrubber Water	TR	≤0.9	NA	≤0.9
Make Up Nitric Acid	≤0.2	1.8	≤0.3	≤0.3
Sodium Hydroxide	39.4	≤0.3	NA	NA
TOTAL	≤67.2	≤16.5	≤28.2	≤27.7
Output Stream Quantity, g atom				
Anolyte	1.3	0.6	≤1.3	≤1.1
Catholyte	1.2	3.5	≤0.9	8.4
NOx Scrubber Effluent	4.2	≤1.3	≤1.0	≤0.3
Scrubber Effluent	3.6	0.4	TR	0.1
Stack Gas	3.7	≤108.5	TR	TR
Anolyte Filter Solids	NA	TR	TR	NA
TOTAL	14	≤114.3	≤3.2	≤9.9

Notes:

1. Species which were reported at below detection limits were calculated with a value equal to detection limit.
2. TR = Trace amounts. Trace amounts were assumed to be 0.
3. NA = Not analyzed

In the HD-4 run, the chloride assay on sodium hydroxide is suspiciously high at 7100 mg/L since the chloride content of the NOx scrubber effluent is so much lower, always less than 100 mg/L. The high stack gas DMSO assays for this run were set by the dilution level of the measurement in the vicinity of 80 mg/dscf, which was very much higher than for any other compound. This probably results in serious overestimation of the stack gas sulfur content. It is of interest to note that some chloride and sulfur containing species showed up in the effluent streams of the GB simulant runs as well, even though none was in the feed recipe and only traces were found in the feed assay. This indicates that the CEROX™ system was not adequately flushed between the two test campaigns although it is unlikely that this condition interfered with system performance. In the GB-4 run the assays of effluent streams either picked up phosphorous/phosphates or DMMP at very low levels or below the limits of detection. It is possible that some of the phosphorous fed to the system was precipitated and circulated through the system in the unsampled and unassayed solids, which may also hold fluoride-containing precipitates.

The lack of assays for nitrate makes it impossible to attempt to close the balance for the nitrogen content of the system. Even if they had been available, however, there would have been problems with assay precision because of the large amount of nitric acid initially charged to the anolyte and catholyte and added subsequently. The same consideration would apply to the system oxygen balances. As described in Section 6.4.2 above, the carbon balances on the system was forced to closure as a device to estimate the actual stack gas flow rate. Inability to close these balances, even approximately, means that estimates of the degree of destruction of the compounds containing them are indigative or inferential at best.

6.4.5 Overall Destruction Efficiency

To calculate an overall destruction efficiency, the total hydrocarbons (TOC) feed can be compared to the TOCs discharged from the unit. Certain assumptions will be made to simplify the calculations as follows:

- Assume gas flow as estimated in Section 6.4.2 (approximately ½ the flow of the reported measurement)
- Ignore accumulation of organics in the anolyte, catholyte, and NOx scrubber solutions. This is based on an assumption that the organic loading in such streams will remain at some equilibrium concentration and therefore no accumulation would occur. This is probably a valid statement for long term operation and not valid for short term runs.

Using the above assumptions, the TOC destruction efficiency can be calculated for the 24 hr tests for runs H-4 and G-4. A TOC destruction efficiency of 98% and 99% for HD and GB neutralent simulants respectively can be seen in Table 6-16.

Table 6-16 TOC Destruction Efficiency

Run Number	**H-2 8-hr**	**H-3 8-hr**	**H-4 24-hr**	**G-2 8-hr**	**G-3 8-hr**	**G-4 24-hr**
Inflow						
Feed, kg TOC	3.33	4.22	11.95	3.60	3.31	9.92
TOTAL IN	3.33	4.22	11.95	3.60	3.31	9.92
Outflow						
Stack Gases, kg TOC	0.060	0.080	0.252	0.029	0.028	0.0689
Scrubber Effluent, kg TOC	0.0134	0.0066	0.0324	0.0050	0.0605	0.0148
TOTAL OUT	0.073	0.086	0.284	0.034	0.088	0.0837
TOC Destruction Efficiency	98%	98%	**98%**	99%	97%	**99%**

7. CONCLUSIONS

Test data and observations from the six Validation test runs using two NSCMP MEA-based neutralent simulants completed as part of the Limited Engineering Scale Testing of the CerOx Process were evaluated in accordance with the test criteria. The technology was evaluated based on four test objectives. The conclusions are summarized below under each listed objective.

1. **Demonstrate stable operability at maximum continuous throughput.**
   - The CerOx System 2 showed stable operation and processed 1.4 and 2.4 kg/hr of HD neutralent simulant and GB neutralent simulant respectively for up to 24 hours.
   - The liquid effluent generated consistently fell below the 25 ppm TOC (Total Organic Carbon) test criteria and generally ranged from 2 to 6 ppm TOC.
   - Estimates of overall destruction were based on the most reliable data, namely TOC concentrations on influents and effluents. The results of these calculations showed destruction efficiencies which ranged from 97 to 99%.
   - During the validation testing, stack gases were estimated at 71-73 dscfm, scrubber effluent ranged between 0.6 and 1.5 gpm, and generated solids amounted to less than a couple of grams recovered from the anolyte solution.
2. **Demonstrate the fate of relevant heteroatoms (F, Cl, S, and P) contained in the feed material.**
   - The data gathered were insufficient to determine elemental material balances for relevant heteroatoms due to analytical difficulties and inaccurate flow measurements.
3. **Provide basic engineering data to evaluate practicality for implementation in NSCMP.**
   - The test data show that a CerOx System 2 of the configuration tested, modified to address certain concerns identified (see below), could process about 2500 gallons of NSCMP HD neutralent or about 4300 gallons of NSCMP GB neutralent per year assuming 80% stream factor.
   - The CerOx System 2 tested is best described as an early commercial system used for research purposes, which did not reflect the best design for the destruction of NSCMP neutralents. This unit initially showed some instability, which was quickly recognized and corrected. CerOx was able to run two 24 hour continuous tests under stable operations, one for each feed. Shortcomings in the tested system included inadequate Gas Phase Reactor and off-gas treatment designs. CerOx latest generation technology, of which a System 4 has been manufactured and delivered to UCI, addresses these design issues.
4. **Quantify and document key operating and engineering design parameters.**
   - The CerOx technology could be designed to process waste equivalent to the production rate of expected NSCMP neutralents. Scale up is directly proportional with area of the electrodes in electrochemical cells. The scale up of other core technology, including the Liquid and Gas Phase Reactors, would be by residence time using standard engineering practices and fundamentals. During operation, temperature, pH, cerium +3/+4 concentration, acid concentration, cell voltage, etc. require monitoring, but very little control.

During the testing, there were a number of issues that developed or were identified. The key ones are listed below:

- In two of the test runs, 0.69 to 1.9 mg/L 1,2-dichloroethane (DCE) was reported in the liquid effluent. DCE is regulated as a toxic contaminant under RCRA's TCLP at a concentration of 0.5 ppm or greater. The CerOx System Liquid and Gas Phase Reactor has since been modified to increase the system's ability to destroy VOCs such as 1,2-dichloroethane. Based on the test results, the liquid effluent generated by the CerOx System (with modifications) is likely to require minimal, if any, treatment prior to discharge. Note that DCE is an ingredient in the simulant feed and not expected to be found in actual NSCMP HD neutralent.

- CerOx Test data show that small quantities (less than a couple of grams) of solids are recovered in the anolyte solution. There was insufficient data to characterize these solids for RCRA requirements. This must be addressed in future testing.
- Stack gas velocities were measured using a single pito tube with questionable accuracy. The stack gases were adjusted based on the carbon mass balance.
- No NSPS or NESHAPs or its associated MACT standards have been established that would apply directly to the CerOx technology. If it is assumed that the NESHAP for Hazardous Waste Combustor (MACT standards) would apply to the CerOx System 2, then CO, THC, HCl and Cl_2 would all fall below their respective allowable limits and none would be considered a major HAP source. Modifications to the existing design are required to increase the efficiency of the Gas Phase Reactor, NOx Absorbers, and Acid Gas Scrubbers to further reduce the emissions of THC, NOx, HCl, and Cl_2 that could come from a NSCMP application. CerOx has stated that such modifications have been incorporated in the recently manufactured CerOx System 4, which was purchased by the University of California, Irvine. A new source of NOx equivalent to the CerOx system tested would not typically be significant enough to trigger major source permit and control technology requirements.
- Process wastes are generated including anolyte and catholyte solutions. These electrolyte solutions would be considered characteristic hazardous wastes and would have to be recycled/reclaimed or disposed of by a facility permitted under RCRA to receive and treat hazardous wastes. The tests performed did not attempt to determine the useful life of the anolyte and catholyte solutions, but were changed between test campaigns per the test plan.
- The data gathered to determine destruction efficiency were insufficient due to analytical difficulties and inaccuracies in flow measurement.

8. RECOMMENDATIONS

Based on the test results, it is recommended that a detailed evaluation of the latest generation CerOx technology be performed to determine if issues identified during the testing have been addressed and if further testing is appropriate.

9. ACRONYMS & ABBREVIATIONS

ACRONYMS & ABBREVAITION	DEFINITIONS
ACWA	Assembled Chemical Weapons Assessment
ATAP	Alternative Technologies and Approaches Program
CEM	Continuous Emission Monitoring
COC	Chain-of-Custody
CWM	Chemical Warfare Materiel
DC	Direct current
DCE	1,2-dichloroethane
DIMP	Di-isopropyl methylphosphonate
DMMP	Dimethyl methylphosphonate
DMSO	Dimethyl sulfoxide
EH&S	Environmental Health and Safety (Department of UNR)
EOR	End of run
GB	Chemical agent, Nerve agent, Sarin
gpm	U.S. Gallon per minute
H	Chemical agent, Sulfur Mustard
HAP	Hazardous Air Pollutants
HD	Chemical agent, Sulfur Mustard (distilled)
HN	Chemical agent, Nitrogen Mustard
LEST	Limited Engineering Scale Testing
MACT	Maximum Achievable Control Technology
MEA	Monoethanolamine
MEO	Mediated Electrochemical Oxidation
MMD	Munitions Management Device
NESHAP	National Emission Standards for Hazardous Air Pollutants
NSCMP	Non-Stockpile Chemical Materiel Program
NSDWR	National Secondary Drinking Water Regulations
NSPS	New Source Performance Standards
ORP	Overarching Research Plan
PFD	Process Flow Diagram
PMCD	Program Manager for Chemical Demilitarization
PNNL	Pacific Northwest National Laboratory
POTW	Publicly Owned Treatment Works
PP	Polypropylene
ppm	Parts per million
$ppm_{v,d}$	Parts per million by volume – dry basis
PSD	Prevention of Significant Deterioration
PTFE	Polytetrafluoroethylene (Teflon®)
PVC	Polyvinyl chloride
PVDF	Polyvinylidene Fluoride

ACRONYMS & ABBREVAITION	DEFINITIONS
RACT	Reasonably Available Control Technology
RCRA	Resource Conservation and Recovery Act
RRS Red	Rapid Response System neutralent of chemical agents HD, HX and Lewisite
SCADA	Supervisory Control and Data Acquisition
SOR	Start of run
SVOC	Semi-volatile organic compound
SwRI	Southwest Research Institute
TCLP	Toxicity Characteristic Leaching Procedure
THC	Total Hydrocarbon
TIC	Total Inorganic Carbon
TMDL	Total Maximum Daily Loading
TOC	Total Organic Carbon
TON	Total Organic Nitrogen
TOX	Total Chlorinated Organic Compound
TRC	TRC Environmental Corporation
TSS	Total Suspended Solids
UCI	University of California at Irvine
UNR	University of Nevada at Reno
VOC	Volatile Organic Compound

10. REFERENCE

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